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ERRATUM.

Vol. 118 (Abstr., 1920).

Page   Line
ii. 298   10 *for* "**Rusting**" *read* "**Roasting.**"

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ERRATA.

Page.	Line.	
475	13	for " s " read " S ."
„	14	„ " $9\eta s$ " read " $9\eta S$."
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476	1	„ " 0·15 cm." read " 0·1588 cm."
„	15	
478	10	„ " 6·69 " read " 6·69 × 19·4."
661	12	„ " sodium sulphate " read " sodium hydrogen sulphate."
832	6	„ " lead acetate " read " sodium plumbite."

ii. 366	20	for " tetradinite " read " tetradymite."
„	„	„ " grunlingite " read " grünlingite."

ii. 337	14*	for " Aktiebolsg " read " Aktiebolag."

ii. 441	23	for " Uto " read " Utö."
„	„	„ " Foren." read " Fören."
„	25	„ " $p - v$ " read " $\rho - v$."
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CONTENTS

ERRATA.

LXXXIX.—*The Viscosity of Solutions of Nitrocellulose in Mixtures of Acetone and Water.*

By Irvine Masson and Robert McCall.

HE viscosity of sols of "soluble" nitrocellulose in ether–alcohol ixtures has been studied by Gibson and McCall (*J. Soc. Chem. id.*, 1920, **39**, 172T). The work summarised in the present paper eals mainly with mixtures of nitrocellulose with acetone, pure and queous, which are of interest from the point of view of their ehaviour as typical colloidal solutions.

The viscosimeter used was that designed by Gibson and Jacobs [this vol., p. 473), in which is measured the rate of fall of a small phere through the solution.

For the experiments with dry nitrocellulose in anhydrous cetone, it is necessary to dry the solvent by prolonged contact rith calcium chloride, followed by fractional distillation with xclusion of water vapour, owing to the marked effect of traces of noisture on viscosity. It is noteworthy that the crystalline com-)ound formed between acetone and calcium chloride (compare 3agster, T., 1914, **105**, 494), which is soluble in anhydrous acetone, las a very marked effect in coagulating sols of nitrocellulose; thus icetone fully dried over calcium chloride, but separated from it oy filtration alone, formed with 5 per cent. of nitrocellulose a stiff jelly having an apparent viscosity of 5000 C.G.S. units, whereas when separated from the calcium chloride by distillation, the acetone gave a mobile sol, the viscosity of which was 13 units. The presence of a little water largely counteracts this coagulating effect, whence it appears that hydrated calcium chloride differs in this respect from the acetone compound. This might repay investigation from the point of view of the coagulation of aqueous sols by electrolytes.

Change in Viscosity with Time.

For consistent results to be obtained, the mixtures must be nade up with the aid of very vigorous initial agitation, followed w mechanical shaking, until uniformity of composition is attained; and in studying these conditions, it was found that there is a very slow decrease of viscosity with time, even after the shaking is ended. With ether–alcohol sols, a much more rapid effect in the opposite direction was observed by Gibson and McCall

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(*loc. cit.*), and such changes have often been noticed with other colloidal systems.

Further measurements have therefore been made with acetone and with mixtures of ether and alcohol. With acetone, either anhydrous or aqueous, the viscosity rises rapidly within a few minutes of mixing to a maximum value, and then falls very gradually, and the same is found to be true with the particular mixture of ether and alcohol in which the nitrocellulose has its lowest viscosity. The more widely, however, the composition of this solvent deviates from this "optimum" value, the longer is
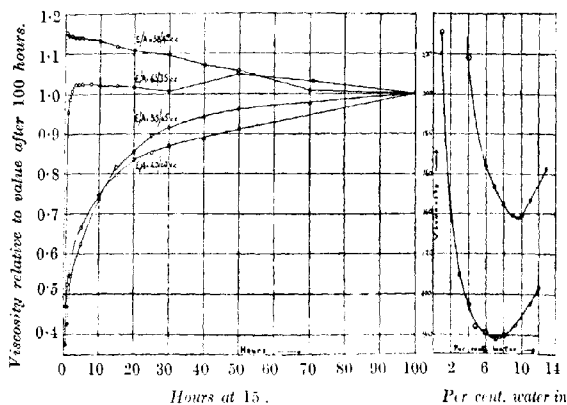
FIG. 1.—*Change of viscosity with time at 15 . Nitrocellulose (N = 12·2 per cent.) 6 grams ; ether-alcohol 100 grams.*

FIG. 2.—*Effect of water on viscosity in acetone. Nitrocellulose 10 grams ; solvent, 100 grams.*

the time taken by the solution to arrive at its highest viscosity. These facts are illustrated in Fig. 1.

It appears that two processes are at work, first, the absorption of solvent by nitrocellulose, accompanied by the dispersion of the resulting gel ; secondly, a change in the already dispersed gel, which may probably be ascribed to a change in the state of aggregation of the particles, not necessarily accompanied by any alteration in their percentage composition. With acetone, and with ether-alcohol near the "optimum," the former process is very rapid ; with other ether-alcohol mixtures the absorption of solvent, with resulting swelling of the particles and decrease in the volume

of the surrounding fluid, continues for some time, even after the primary dispersion has occurred. In all cases, the second process is very slow.

Influence of Water on Viscosity.

Measurements were made at 20° of the viscosities of a number of kinds of nitrocellulose in acetone to which varying proportions of water had been added; some typical results at various concentrations are shown in table I and in Fig. 2. It will be seen that the viscosities in anhydrous acetone are relatively very high, and that

TABLE I.

Absolute Viscosities at 20° in Acetone and Water.

Concentrations in grams per 100 grams of acetone and water. Italicised numbers show minimum viscosities.

Percentage of water.	N=12·3 per cent.				N=13·0 per cent.		
	5.	7.	8·5.	10.	5.	7.	10.
0	—	—	—	—	12·5	—	—
1	34·2	213·2	—	—	8·8	32·0	232
2	—	—	—	451	—	26·4	—
3	11·7	62·5	157·3	—	6·1	—	110
4	—	—	—	218	6·0	20·8	96·4
5	8·6	41·4	90·5	—	6·0	—	83·3
6	8·2	36·7	74·6	164	*5·9*	*20·2*	81·1
7	8·0	33·8	73·8	154	*5·9*	20·7	*79·3*
8	*7·9*	32·9	72·5	144	*5·9*	21·4	79·7
9	*7·9*	*32·7*	*69·3*	138	—	23·0	83·3
10	8·1	35·5	71·4	*133*	6·6	24·6	—
11	8·0	—	72·7	147	—	—	94·9
12	—	36·6	75·7	—	7·3	28·2	103
13	9·1	—	79·9	163	7·1*	—	120
14	—	40·2	—	—	—	—	—
15	8·6	—	—	154*	—	—	—
16	—	47·6*	—	—	—	—	—

* Miscibility incomplete.

traces of water have a most marked effect in lowering viscosity. The influence of water diminishes with further addition, until in mixtures still more aqueous the viscosity again rises. There is thus an optimum solvent composition at which the viscosity is at a minimum. When upwards of 12 per cent. of water is present in the acetone (the exact figure depending on the type and concentration of nitrocellulose), the liquid will no longer permit the dispersion of the nitrocellulose, but it still causes gelatinisation, to an extent depending on the water content. The optimum solvent-composition (by make-up) is not the same for all kinds of nitro-

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cellulose, nor is it quite independent of concentration. With sols in pure acetone, no appreciable concentration of dissolved matter was detected by ordinary vapour-pressure measurements, and the disperse phase presumably consists of particles of nitrocellulose gel containing absorbed solvent. The proportion of liquid dissolved by nitrocellulose is large; gels collected from highly aqueous acetone contained more than six times as much liquid as solid, whilst other tests showed still greater absorption with mixtures capable of dispersing the material.

Not only the quantity, but also the composition of the absorbed fluid, is found to be affected by the composition of the binary solvent; selective absorption by the gel is at work, hence the composition of the fluid phase at equilibrium is not necessarily the same as that of the solvent before admixture with nitrocellulose. These factors play a leading part in determining the viscosity of such systems as are here dealt with; their quantitative influence has yet to be studied.

Influence of Concentration on Viscosity.

The correlation of the viscosity of sols with the concentration of the disperse phase has attracted the attention of numerous workers; Einstein, also Hatschek (*Trans. Faraday Soc.*, 1913, **9**, 80, with list of references), have obtained an equation founded on theoretical considerations, whilst Arrhenius (*Biochem. J.*, 1917, **11**, 112) has successfully applied an empirical logarithmic expression to numerous cases in which the Einstein-Hatschek expression fails. Baker (T., 1913, **108**, 1653) studied dilute sols of nitrocellulose in acetone, and his data were examined by Arrhenius.

In table II are given some of the results now obtained. Examination of the data shows that none of the equations referred to is applicable except over small ranges, and this is true whether anhydrous or aqueous acetone be used as the solvent. It should be added that Hatschek's second expression (*loc. cit.*), for cases where the disperse phase occupies most of the total volume, does not apply to the present data, and, indeed, it cannot hold for any case in which the viscosity is great compared with that of the solvent.

TABLE II.

Viscosities at 20° in Anhydrous Acetone.

Nitrocellulose, N = 13·0 per cent.			Nitrocellulose, N = 12·2 per cent.	
Grams per 100 grams of acetone	D_4^{20}.	Viscosity (absolute).	Grams per 100 grams of acetone.	Viscosity (absolute).
—	0·792	0·0033*	—	—
0·63	0·794	0·0602*	4·43	35·5
5·05	0·814	13·9	5·05	117·0
5·68	0·817	25·1	5·68	305·0
6·31	0·820	42·7	6·31	867·0
6·94	0·823	67·8	—	—
7·58	0·827	106·7	—	—

* Determined with Ostwald viscosimeter.

No quantitative theory can apply to the viscosity of emulsoids which does not take into account the fact that the tangential stress, expressed by the viscosity, must in part be expended in keeping the dispersed particles deformed against the forces due either to interfacial tension (liquid emulsions) or to the internal elasticity of the particles (dispersed gels); and in view of our ignorance of the shapes assumed by such particles under shear, the problem appears highly complex.

The authors' thanks are due to Mrs. B. Clemmow, B.Sc., and Miss D. S. Jones for their assistance; to the Director of Artillery for his permission to publish; to the Superintendent of Research, Woolwich, and to Sir Robert Robertson, F.R.S., for their interest in the work.

UNIVERSITY COLLEGE, LONDON.
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XC.—*The Electrical Conductivity of Pure Salts in the Solid and Fused States. Determination of the Activity-coefficients of Ions in Solid Salts.*

By JNANENDRA CHANDRA GHOSH.

RECENT researches on X-ray analysis of crystal structure have proved conclusively that the atoms of a salt are arranged symmetrically in a space-lattice. Debye and Scherrer have also considered the possibility of ionisation in crystals of electrolytes (*Physikal. Zeitsch.*, 1918, **19**, 474). They assume that the diffract-

ing power of an atom depends on the number of electrons in the atom. This is equal to the Moseley number in a neutral atom. From the effective reflecting values of planes alternately wholly lithium and wholly fluorine, in a crystal of lithium fluoride, they conclude that the lithium atom has lost, and the fluorine atom has gained, an electron. Thus the internal ionisation of a solid salt is always complete.

Although ionisation is complete, the ions are not free to glide past one another, because of the great magnitude of the forces of cohesion, which prevent the displacement of an ion from its position of equilibrium in the crystal lattice. It is only at high temperatures, when the average kinetic energy of the ions has become sufficiently great for some of them to overcome this field of elastic force, that the electrical conductivity of the solid salt is observed. The number of free ions in a uni-univalent salt is given by the equation

$$2\,n = 2N\,.\,e^{-\frac{W}{2kT}} \qquad \ldots \ldots \quad (1)$$

where N is Avogadro's number and W may be defined as the work that the ions of a gram-molecule must perform against the forces of elasticity before they can be free to glide past one another at the absolute temperature, T. On the assumption that Ohm's law is always valid, the specific conductivity is given by the equation

$$\mu = \frac{2n}{v}\,.\,U \qquad \ldots \ldots \quad (2)$$

where v is the molecular volume of the salt and U the average mobility of the ions at T, or

$$\mu = \frac{U}{v}\,2Ne^{-\frac{W}{2RT}} \qquad \ldots \ldots \quad (3)$$

Variation of W with Temperature.

The transition of ions from the bound to the free state inside the solid salt may be considered as a physico-chemical process attended with an absorption of energy, W, for each gram-molecule. In a condensed system, the variation of the energy of transition with temperature is given by the equation

$$W = W_0 + \beta T^2 \qquad \ldots \quad \text{Nernst theorem} \quad (4)$$

It appears plausible that equation (4) may be valid in this particular case. The nature of the forces operating in the interior of a solid salt is practically unknown, and can only be considered in a general way. Larmor has investigated the case of a fluid

composed of finite particles, and concludes that the force at an internal point, due to particles surrounding the point, is separable into two parts, one being due to the medium as a whole and the other a purely local part. The first part can be determined, as it depends on the potential due to the combined volume and surface-density distributions of Poisson. For an isotropic liquid, the second part can be easily neglected, as the particles are in a state of violent, irregular motion, and their axes are distributed quite haphazardly. In the case of a crystal, however, there is a definite geometrical configuration. The atoms, arranged in a space-lattice, immediately surrounding the point, give rise to a purely local force at that point. So long as the crystalline structure is maintained, the motion of the particles is not random, and there is no cancelling out of the forces due to each particle. The magnitude of W depends on the purely local part of the forces at an internal point, and from its very nature remains unknown. It is fairly certain, however, that it runs parallel with the forces of elastic rigidity inside a solid. It is well known that the plasticity of crystalline substances increases very rapidly with temperature, hence W diminishes with increasing temperature. β has thus a negative sign. At the melting point, where the purely local part of the forces is negligibly small, we may assume that

$$W = W_0 + \beta T_m{}^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where T_m is the melting point of the salt.

β can thus be easily expressed in terms of W_0 being equal to

$$- \frac{W_0}{T_m{}^2}.$$

Therefore at any temperature, T,

$$W = W_0 - \frac{W_0 T^2}{T_m{}^2} = W_0 \left\{ 1 - \frac{T^2}{T_m{}^2} \right\} \quad . \quad . \quad . \quad (6)$$

Variation of the Mobility of the Ion of a Solid Salt with Temperature.

The variation of the mobility of an ion in a solid with rise in temperature can be easily accounted for in a way analogous to that developed in the electron theory of metallic conduction. If X is the strength of the electric field, the force acting on an ion is Xe. If the ion were perfectly free to move, there would be a constant acceleration of $\frac{Xe}{m}$ in the direction of the field, where m is the mass of the ion. There are, however, frequent collisions

with other ions, when all the accumulated energy of the ion is lost. It may be considered as the criterion of the solid state that the whole of the velocity of the free ion, added by the electric field, is removed at each collision, and the ion starts its course again with zero velocity. Let τ be the time taken by the ion to describe the mean free path, L. The velocity of the ion at the end of the mean free path due to the electrical field is $\dfrac{Xe\tau}{m}$.

Therefore the average velocity added by the field in its own direction:

$$U' = \frac{1}{2} \cdot \frac{Xe\tau}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If V is the speed of the ion due to the combined effect of the electrical field and thermal agitation, then $\tau = \dfrac{L}{V}$. Since, however, the velocity of thermal agitation is very large compared with the velocity added by the electrical field, the value of V will be almost equal to V'', the velocity due to thermal agitation alone. Therefore

$$U' = \frac{1}{2} \cdot \frac{Xe}{m} \cdot \frac{L}{V''}$$

$$V'' = \sqrt{\frac{3 \cdot RT}{M}}$$

so that

$$U' = \frac{1}{2} \cdot \frac{e}{m} \cdot \frac{L}{\sqrt{3 \cdot R \cdot \dfrac{1}{M} \cdot T}} \cdot X \quad . \quad . \quad . \quad (8)$$

Now $L = \dfrac{\lambda^3}{\frac{4}{3}\pi S^2}$, where λ is the mean distance of the supposedly spherical ions and S the distance between the centres of gravity of two ions in collision. Since the coefficient of cubical expansion is negligibly small, L may always be regarded as constant.

Hence

$$U' = \frac{k'}{\sqrt{T}} \cdot X$$

or the mobility

$$U = \frac{k'}{\sqrt{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Variation of the Specific Conductivity of a Solid Salt with Temperature.

Substituting the values of U and W from equations (9) and (6) respectively, in equation (3) we get

$$\mu = \frac{k'}{v} \cdot \frac{1}{\sqrt{T}} \cdot 2N \cdot e^{-W_0\left\{1 - \frac{T^2}{T_m^2}\right\}/2RT} \quad . \quad . \quad (10)$$

Since the change in molecular volume with temperature is negligible in the case of a solid,

$$\mu = \frac{k}{\sqrt{T}} \cdot 2N \cdot e^{-W_0\left\{1 - \frac{T^2}{T_m^2}\right\}/2RT}$$

or

$$\frac{W_0\left\{1 - \frac{T^2}{T_m^2}\right\}}{2RT} = \log_e 2N \cdot K/\mu\sqrt{T} \quad . \quad . \quad (11)$$

or

$$\frac{W_0(T_2 - T_1)}{2R} \left\{\frac{1}{T_1 T_2} - \frac{1}{T_m^2}\right\} = \log_e \frac{\mu_2 \sqrt{T_2}}{\mu_1 \sqrt{T_1}} \quad . \quad . \quad (12)$$

Equation (12) contains only one unknown constant, W_0, which can be easily obtained from any two values of μ. In the following tables, it will be seen how satisfactorily the above equation reproduces the observed values of μ. Column 4 of these tables contains the values of a —the activity-coefficient of the ions of a solid salt at various temperatures. They are calculated from equation (1):

$$\frac{W}{2RT} = \log_e \frac{2N}{2n} = \log_e \frac{1}{a} \quad . \quad . \quad . \quad (13)$$

or

$$\frac{W_0\left\{1 - \frac{T^2}{T_m^2}\right\}}{2RT} = \log_e \frac{1}{a} .$$

It will be noticed that the specific conductivity of the salts in some cases has increased almost a thousand times, but throughout this range, values of a calculated from equation (12) agree with the observed values within 5 per cent. The observed specific conductivities in the case of sodium and potassium chlorides are taken from the work of Benrath and Wainoff (*Zeitsch. physikal. Chem.*, 1911, **77**, 257). The limits of experimental error, according to their own statement, are ±10 per cent. The data for the haloids of silver and thallium are obtained from the work of Tubandt and Lorenz (*Zeitsch. physikal. Chem.*, 1914, **87**, 529).

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TABLE I.

Sodium Chloride.

$W_0 = 51\cdot2$ kg. cal. $T_m = 1083$ absolute.

T (absolute).	μ calc. $\times 10^6$.	μ obs. $\times 10^6$.	a calc.
903	—	12·6	0·0127
923	21·2	21·2	0·0216
943	35·4	35·0	0363
983	91·0	95·0	0988
1023	240·0	240·0	0·2551
1073	729·0	729·0	0·8034

TABLE II.

Potassium Chloride.

$W_0 = 50\cdot9$ kg. cal. $T_m = 1063$.

T.	μ calc. $\times 10^6$.	μ obs. $\times 10^6$.	a calc.
923	—	6·5	0·0324
933	8·4	8·4	0·0423
983	29·2	28·8	0·1469
1013	59·6	59·6	0·3095
1043	120·0	133·0	0·6295

TABLE III.

Silver Chloride.

$W_0 = 25\cdot6$ kg. cal. $T_m = 726$.

T.	μ calc.	μ obs.	a calc.
523	—	0·0003	0·0026
573	0·0016	0·0015	0·0112
623	0·0068	0·0065	0·0645
673	0·0260	0·0260	0·2587
723	0·0980	0·1100	0·9292

TABLE IV.

Silver Bromide.

$W_0 = 24\cdot8$ kg. cal. $T_m = 690$.

T.	μ calc.	μ obs.	a calc.
473	—	0·00052	0·00089
513	0·00238	0·00230	0·00427
553	0·01000	0·00910	0·01731
623	0·08000	0·08000	0·15600
673	0·36600	0·38000	0·63720

TABLE V.

Thallous Chloride.

$W_0 = 23\cdot75$ kg. cal. $T_m = 700$.

T.	μ calc.	μ obs.	a calc.
523	—	0·00005	0·00625
573	0·00024	0·00024	0·03162
623	0·00098	0·00090	0·23310
673	0·00360	0·00370	0·50870
694	0·00600	0·00610	0·86140

TABLE VI.

Thallous Bromide.

$W_0 = 21\cdot67$ kg. cal. $T_m = 730$.

T.	μ calc.	μ obs.	a calc.
523	—	0·00004	0·00612
623	0·00055	0·00055	0·09204
673	0·00170	0·00160	0·29510
720	0·00440	0·00470	0·81280

TABLE VII.

Thallous Iodide.

$W_0 = 18\cdot7$ kg. cal. $T_m = 710$.

T.	μ calc.	μ obs.	a calc.
523	—	0·0001	0·0160
623	0·0010	0·0010	0·1747
673	0·0027	0·0027	0·4898
702	0·0046	0·0048	0·8567

Electrical Conductivity of Fused Salts.

It follows from equation (6) that at the melting point all the ons are free to glide past one another, since W is zero at this .emperature. Indeed, the belief is held generally that the activity-oefficient of fused salts is always unity. Thus, on considerations based on the molecular kinetic theory of Einstein, Lorenz draws the conclusion that fused salts are completely split up into free-moving ions ("Nernst Festschrift." p. 226. Halle, 1912). In the case of univalent molten salts, Arndt (*Zeitsch. Elektrochem.*, 1907, **13**, 510, 809) drew the same conclusion on the basis of investigations relating the viscosity with the molecular conductivity of the fused salt. Thus the specific conductivity of fused salts does not vary with temperature in a logarithmic way. This is to be expected, as all the ions present contribute to the conduction of electricity. As a general rule, the equation

$$\mu_2 = \mu_1\{1 - a(t_2 - t_1)\} \quad \cdots \quad \cdots \quad (14)$$

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is found to express satisfactorily the variation of conductivity with temperature, indicating that it is a simple case of variation of the mobility of the ion.

My best thanks are due to Prof. F. G. Donnan, F.R.S., for his suggestions and kind interest, and also to my friend, Mr. J. N. Mukherjee.

XCI.—*The Constitution of Yellow Sulphide Dyes.*

By JATINDRA KUMAR MAZUMDER and EDWIN ROY WATSON.

THE following experimental work is recorded as the authors will have no further opportunity for joint work on this subject. Unfortunately, the results obtained are as yet insufficient to allow of deductions as to the constitution of these dyes.

Hitherto, no investigation on this subject appears to have been recorded. From analogy to the formation of dehydrothiotoluidine and primuline base from sulphur and *p*-toluidine, and because yellow sulphide dyes cannot be formed from *m*-phenylenediamine and sulphur, but are formed from the sulphur fusion of *m*-tolylene diamine or acyl derivatives of *m*-phenylenediamine, it has been generally supposed that these dyes contain thiazole rings. From these ideas, one would naturally expect a considerable number of free amino-groups in the simplest sulphide dye, for example, that formed from the sulphur fusion of *m*-tolylenediamine,
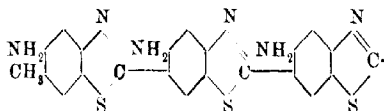
One of us found, however, that the reaction of yellow sulphide dyes with nitrous acid, either in concentrated sulphuric acid solution or freshly precipitated and in aqueous suspension, is inappreciable, and this observation led to the present investigation.

Preparation and Analysis of the Dye.

Attempts to prepare what one would suppose to be the simplest yellow sulphide dye by the fusion of *m*-tolylenediamine and

sulphur according to D.R.-P. 139430 and 141576 gave a product with poor tinctorial properties, but a good yellow dye was obtained from the diformyl derivative of m-tolylenediamine by sulphur fusion according to D.R.-P. 138839, and this was used for the present investigation. The fusion product was extracted with carbon disulphide, dissolved in hot dilute sodium hydroxide solution, precipitated by hydrochloric acid, collected, washed, dried, and again extracted with carbon disulphide (Found: C*=41·5, 41·6, 41·4; H=$\text{\textbf{4}}$·2, 2·7, 2·5; N=9·5, 13·4, 11·0,† 11·7†; S=42·3, 44·6, 42·8).

Nitrogen was evolved very slowly in the estimation by Dumas's method, and the results were consequently untrustworthy. The figures obtained by Kjeldahl's method may be taken to indicate the lowest possible value of the percentage of nitrogen.

Another sample was exhaustively extracted with carbon disulphide, but was not dissolved in alkali and reprecipitated. These steps were omitted in order to avoid the introduction of impurities, as it was found that the reprecipitated substance filtered with difficulty and could not be easily washed (Found: C=42·9; H=2·98; S=42·3).

These figures indicate that the substance contains no oxygen. The proportion of carbon to nitrogen is less than in diformyl-m-tolylenediamine, $C_9H_{10}O_2N_2$, but greater than in m-tolylenediamine, $C_7H_{10}N_2$. $[(C_{17}H_{14}N_4S_{6\cdot27})_n$ requires C=42·98; H=2·95; N=11·8; S=42·27 per cent.]

On account of the tendency of sulphur to form polysulphide chains with any number of sulphur atoms, such a formula probably expresses the composition more correctly than one containing an integral number of sulphur atoms, but agreeing less closely with the analytical results.

Experiments on the Formation of Dye with varying Proportions of Diformyl-m-tolylenediamine and Sulphur.

The mixture was in each case heated according to D.R.-P. 138839. The products were finely powdered and washed in succession with carbon disulphide and water.

Expt. (1).—Two parts of diformyl compound and 4 parts of sulphur gave 3 parts of dye.

Expt. (2).—Two parts of diformyl compound and 2 parts of sulphur gave 1·9 parts of dye.

* C. H. and S determined together by Dennstedt's method.
† By Kjeldahl's method.

Expt. (3).—Two parts of diformyl compound and 1 part of sulphur gave 1·05 parts of dye.

In Expt. (1), the proportions are those specified in the patent. The product from Expt. (2) was an equally strong dye, but that from (3) was much weaker.

Lead Salt.—On adding a solution of lead acetate to a solution of the dye in dilute sodium hydroxide, there was obtained a brown precipitate. This filtered very badly, but was washed first by decantation. (Found: Pb=51·0, 51·1. $C_{17}H_{10}N_4S_{8·27}Pb_2$ requires Pb=46·8 per cent.).

This result seems to indicate that there are approximately two mercaptan or acidic groups for each molecule of diformyl-*m*-tolylenediamine which has entered into the formation of the dye.

Oxidation of the Dye in Alkaline Solution with Potassium Permanganate.

One gram of the dye was dissolved in a solution of 2·5 grams of potassium hydroxide in 20 c.c. of water, and a solution of 2·5 grams of potassium permanganate in 50 c.c. of water was gradually added while the mixture was kept cool. The permanganate was immediately destroyed. The mixture was boiled and filtered hot, and the residual manganese dioxide was extracted with boiling water. On concentrating the filtrate and washings to 25 c.c. and acidifying with hydrochloric acid, sulphur dioxide was evolved, and a red precipitate was obtained, which was collected. Nothing was extracted from the filtrate by shaking with ether. The precipitate was washed with cold water and dried, first on a tile and then in an air-oven at 120° (analysis No. 1). It is somewhat soluble in cold, and almost completely so in hot, water. With the idea of preparing a purer sample for analysis, the precipitate from another preparation was boiled with excess of water and filtered hot, the filtrate was evaporated to dryness, and the residue dried in the air-oven for analysis (No. 2). This gave, however, a large quantity of ash, so it was washed with dilute hydrochloric acid and again dried and analysed (No. 3).

(1) C=42·5; H=3·57; S=29·2.
(2) C=41·7; H=4·5; S=32·1.
(3) C=42·1; H=3·1; S=24·9; N=11·7.

The samples contained 4·25 and 4·3 per cent. of ash respectively. The percentages are reckoned on ash-free substance.

$C_9H_8O_3N_2S_2$ requires C=42·2; H=3·1; N=10·9; S=25·0.
$C_{17}H_{14}O_3N_4S_{3·69}$ requires C=43·2; H=2·96; N=11·8; S=25·0
per cent.

The latter formula is preferred because it contains the same number of carbon, hydrogen, and nitrogen atoms as the original dye. On the most natural assumption that this substance is a sulphonic acid, we require a complex of at least $(C_{17}H_{14}N_4S_{6\cdot27})_6$ in the dye to explain its formation, which is represented as follows:

$$(C_{17}H_{12}N_4S_2)_6(S\cdot SH)_5(S\cdot S\cdot SH)_5 \longrightarrow (C_{17}H_{12}N_4S_2)_6(SO_3H)_{10}.$$
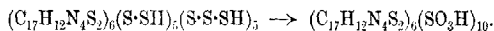
We deduce from this that the dye complex formed from twelve molecules of diformyl-m-tolylenediamine contains five ·S·SH groups and five ·S·S·SH groups, which are all converted into sulphonic acid groups on oxidation. There only remain twelve sulphur atoms for ring-formation, that is, one atom for each molecule of diformyl-m-tolylenediamine. According to this, only half the nitrogen can be involved in thiazole rings.

These conclusions are apparently opposed to those deduced from the analysis of the lead salt of the dyes, from which we inferred the presence of approximately two mercaptan or acidic groups for each molecule of diformyl-m-tolylenediamine concerned in the formation of the dye. It is just conceivable, however, that other atoms or groups, for example, a nitrogen atom in the ring, may exhibit acid properties.

Bases formed by the Action of Hydriodic Acid and Red Phosphorus on the Dye.

On boiling with these reagents under reflux, there is at first a little evolution of hydrogen sulphide, but, after many hours' boiling, the dye is apparently unchanged. Two and a-half grams were boiled for six hours with 0·8 gram of red phosphorus and 15 c.c. of hydriodic acid (D 1·7). The mixture was then transferred to a thick-walled glass tube, a further 0·8 gram of red phosphorus and 10 c.c. of hydriodic acid were added, the tube was sealed, and heated at 190—213° for eight and a-half hours. Much hydrogen sulphide was produced. The bulk of the hydriodic acid was distilled off, and the residue was distilled with water and filtered. On adding sodium acetate to the filtrate, a bright yellow, flocculent precipitate was formed, which was collected, washed and dried (base A). On adding sodium carbonate to the filtrate and extracting repeatedly with ether, a dark brown, tarry substance was obtained (base B). The amount of A was about 0·25 gram and of B about 0·5 gram.

Base A.—After drying on a porous tile, this melted and decomposed at 180—200°. No crystalline acetyl derivative could be obtained from it. (Found: C 58·5; H 5·6; N 13·96; S 12·2.

$C_{38}H_{44}O_5N_8S_3$ requires $C = 57.9$; $H = 5.59$; $N = 14.2$; $S = 12.2$ per cent.).

Base B.—On one occasion a few crystals were obtained by acetylating with acetic anhydride and pyridine, evaporating to dryness, and crystallising from alcohol. Attempts to obtain more crystals were, however, unsuccessful. This base contained no sulphur (and no iodine). [Found: $C = 61.9$; $H = 7.37$; $N = 8.4$. M.W. $= 314$ (determined by the cryoscopic method in glacial acetic acid solution). $NH_2 = 4.16$ (determined by dissolving in dilute hydrochloric acid and titrating with standard nitrite solution). $C_{17}H_{22}O_5N(NH_2)$ requires $C = 60.7$; $H = 7.14$; $N = 8.33$; $NH_2 = 4.76$ per cent.].

By coupling the diazotised solution with β-naphthol in alkaline solution, a crimson dye was obtained, which was insoluble in dilute sodium hydroxide solution.

The presence of oxygen in these bases was unexpected. Their chemical behaviour seems inconsistent with the presence of hydroxyl or carboxyl groups. The substances were heated to constant weight at about 130° before analysis. However, if we assume the oxygen to be contained in molecularly attached water, the formulæ become $C_{38}H_{34}N_5S_3.5H_2O$ and $C_{17}H_{12}N(NH_2).5H_2O$. In a very approximate way, these formulæ may be interpreted as indicating that the polysulphide groups are first removed, and subsequently the cyclic sulphur is eliminated with half the nitrogen (one atom of nitrogen being removed with each atom of sulphur). As only half the remaining nitrogen is in the amino-form, the other half probably forms part of an unbroken ring connecting two benzene nuclei and not containing sulphur.

The action on the dye of tin and hydrochloric acid, zinc dust and sodium hydroxide, bromine, sodium hypobromite, phosphorus pentachloride, phosphorus pentachloride and phosphoryl chloride, phosphorus trichloride, or hot concentrated sulphuric acid has not given products which seem likely to assist in determining the constitution. Up to the present, nothing of interest has been obtained by the action of nitric acid.

DACCA COLLEGE,
E. BENGAL, INDIA.

XCII.—*The Determination of the Relative Strengths of some Nitrogen Bases of the Aromatic Series and of some Alkaloids.*

By FRANCIS ARNALL.

IN the selection of a method by which to determine the relative strengths of the bases of the aromatic series, it must be borne in mind that on the whole they are feeble bases, and, furthermore, that they are usually almost insoluble in water. On the other hand, the salts of these bases are soluble. The author therefore considered that the most satisfactory method would be to measure the degree of hydrolysis of the hydrochlorides in aqueous solution by observing the acceleration of the rate of inversion of a solution of sucrose by means of the polarimeter. In using this method, care must be taken to ensure the same constant temperature throughout all the experiments. Moreover, since the preparation of the hydrochlorides of many of the bases was not possible, the solutions had to be prepared by the addition of the requisite quantity of acid to the weighed base after careful purification of the latter.

In carrying out an experiment, equal volumes of the sucrose solution (5 grams per 100 c.c.) and the solution of the hydrochloride were brought to 55° in the thermostat, mixed, and rapidly transferred to a well-jacketed polarimeter tube, provided with false ends to check loss of heat by radiation, already maintained at the correct temperature. The first reading was taken as soon as the thermometer was steady, and readings were then made at intervals until the reaction was sufficiently advanced. The "final rotation," when the sugar was completely inverted, was read after the solution had been heated to 80° for fifteen minutes. The degree of hydrolysis of the hydrochloride was deduced from the velocity of reaction by comparison with the velocities of inversion by hydrochloric acid alone.

The degree of hydrolysis having been found at several dilutions, the dissociation constant of the salt, the basic constant of the base, and the relative strength of the base to aniline were calculated. As an example of the results obtained, the following may be given:

Salt.	Dilution = v.	Degree of hydrolysis $= \beta$ at 55°.	Dissociation constant $K_i = \dfrac{\beta^2}{(1-\beta)v}$
Dimethylaniline hydrochloride.	4	0·0098	$2\cdot4 \times 10^{-5}$
	8	0·0133	$2\cdot3 \times 10^{-5}$
	16	0·0189	$2\cdot3 \times 10^{-5}$

A small excess of free hydrochloric acid in the solution of the hydrochloride sometimes improved the clarity of the solution, enabling more accurate readings to be taken, whilst its effect on the degree of hydrolysis was found to be negligible.

Usually, the excess of acid was not more than a small percentage of the acid set free by hydrolysis. For example, diphenylamine hydrochloride in $N/240$-solution was dissociated to the extent of 89 per cent.; the amount of free acid apart from this was $N/2400$. Thus the excess of acid was equal to 11 per cent. of the free acid due to the hydrolysis of the salt. In the case of stronger bases, where the degree of hydrolysis was small, the excess of acid used was of the same order as the free acid due to hydrolysis. Before accepting the results obtained in this way, experiments were carried out with quinoline hydrochloride in order to ensure that this did not invalidate the results.

Concentration of the hydrochloride.	Concentration of the excess acid.	Total free acid in solution.	Degree of hydrolysis. Per cent.
$N/4$	$N/200$	$N/98\cdot9$	2·045
$N/4$	$N/400$	$N/131\cdot2$	2·05

It will be seen that doubling the amount of excess acid did not affect the degree of hydrolysis.

In the case of dimethylaniline, consistent results were only obtained by the use of freshly prepared solutions of the base recently fractionated under diminished pressure, since the solution of the hydrochloride, although prepared with freshly distilled conductivity water and kept in the dark, changed in the course of a few hours to a pale heliotrope colour, even in well-stoppered bottles. Crystalline dimethylaniline hydrochloride could be prepared by passing pure dry hydrogen chloride into a dry ethereal solution of the base, but it was considered preferable to use the solution obtained by the addition of pure acid to the pure base.

The volatility of pyridine rendered the preparation of the hydrochloride solution inaccurate unless great care were taken.

The more common alkaloids, such as strychnine, brucine, cocaine, and morphine, were found to be too strongly basic to give satisfactory results by this method.

The velocity of inversion of the sucrose solution was, even with some of the solutions used, only sufficiently rapid for convenient measurement at the temperature employed, namely, 55°. It was established by experiment that coloration of the sugar solution sometimes occurred on prolonged warming at temperatures a little above 55°.

The following tables summarise briefly the results obtained.

TABLE I.

The Relative Strengths and Basic Constants of the Bases.

Base.	K_s.	$K_b = \dfrac{K_w}{K_s}$.	Aniline $= 100$.
Dimethylaniline	$2\cdot3 \times 10^{-5}$	$5\cdot22 \times 10^{-10}$	430·0
p-Toluidine	$4\cdot0 \times 10^{-5}$	$3\cdot00 \times 10^{-10}$	250·0
m-Xylidine	$8\cdot5 \times 10^{-5}$	$1\cdot41 \times 10^{-10}$	120·0
Aniline	$1\cdot00 \times 10^{-4}$	$1\cdot20 \times 10^{-10}$	100·0
Pyridine	$1\cdot01 \times 10^{-4}$	$1\cdot19 \times 10^{-10}$	99·0
Quinoline	$1\cdot07 \times 10^{-4}$	$1\cdot12 \times 10^{-10}$	93·0
o-Toluidine	$1\cdot59 \times 10^{-4}$	$7\cdot50 \times 10^{-11}$	62·0
m-Aminobenzoic acid	$8\cdot7 \times 10^{-4}$	$1\cdot38 \times 10^{-11}$	11·0
p-Aminobenzoic acid	$9\cdot5 \times 10^{-3}$	$1\cdot26 \times 10^{-12}$	1·1
o-Aminobenzoic acid	$1\cdot63 \times 10^{-2}$	$7\cdot36 \times 10^{-13}$	0·61
Diphenylamine	$2\cdot9 \times 10^{-2}$	$4\cdot14 \times 10^{-13}$	0·34
Aceto-p-toluidide	$3\cdot2 \times 10^{-2}$	$3\cdot75 \times 10^{-13}$	0·31
Benzo-p-toluidide	$4\cdot0 \times 10^{-2}$	$3\cdot00 \times 10^{-13}$	0·25
Aceto-m-4-xylidide	$4\cdot5 \times 10^{-2}$	$2\cdot67 \times 10^{-13}$	0·22
Acetanilide	$4\cdot8 \times 10^{-2}$	$2\cdot50 \times 10^{-13}$	0·21
Aceto-o-toluidide	$5\cdot3 \times 10^{-2}$	$2\cdot26 \times 10^{-13}$	0·19
Benzo-m-4-xylidide	$5\cdot3 \times 10^{-2}$	$2\cdot26 \times 10^{-13}$	0·19
Benzanilide	$5\cdot5 \times 10^{-2}$	$2\cdot18 \times 10^{-13}$	0·18
Benzo-o-toluidide	$5\cdot9 \times 10^{-2}$	$2\cdot03 \times 10^{-13}$	0·17

$K_s =$ hydrolysis constant of the hydrochloride in aqueous solution.
$K_b =$ basic constant.
$K_w =$ dissociation constant for water, assumed to be equal to $1\cdot2 \times 10^{-14}$ for 55°.

TABLE II.

Relative Strengths and Basic Constants of Alkaloids.

Alkaloid.	K_s.	$K_b = \dfrac{K_w}{K_s}$.	Aniline $= 100$.
Quinine	$5\cdot1 \times 10^{-6}$	$2\cdot35 \times 10^{-9}$	2000·0
Narcotine	$4\cdot2 \times 10^{-5}$	$2\cdot86 \times 10^{-10}$	240·0
Cinchonine	$6\cdot1 \times 10^{-5}$	$1\cdot97 \times 10^{-10}$	160·0
Quinidine	$7\cdot5 \times 10^{-5}$	$1\cdot60 \times 10^{-10}$	130·0
Piperine	$3\cdot8 \times 10^{-2}$	$3\cdot16 \times 10^{-13}$	0·26
Caffeine	$6\cdot0 \times 10^{-2}$	$2\cdot00 \times 10^{-13}$	0·17
Theobromine	$8\cdot3 \times 10^{-2}$	$1\cdot45 \times 10^{-13}$	0·12

TABLE III.

Decrease in Basic Strength on forming Acetyl and Benzoyl Derivatives.

Base.	Strength of base.	Strength of acetyl derivative.	Strength of benzoyl derivative.
p-Toluidine	250	0·31	0·25
m-4-Xylidine	120	0·22	0·19
Aniline	100	0·21	0·18
o-Toluidine	62	0·19	0·17

All the values given are relative to aniline = 100.

As would be expected, the benzoyl derivatives are weaker than the corresponding acetyl derivatives, and the order of strength of the bases is also the order of strength of their acyl derivatives.

TABLE IV.

Percentage Degree of Hydrolysis of Hydrochlorides of Bases.

A.

Base.	$v = 100.$	$v = 150.$	$v = 200.$
Acetanilide	—	89·0	91·2
Aceto-o-toluidide	—	90·0	92·0
Aceto-p-toluidide	—	84·9	87·9
Aceto-m-4-xylidide	—	88·2	90·8
Benzanilide	—	90·2	92·4
Benzo-o-toluidide	—	90·6	92·7
Benzo-p-toluidide	—	87·3	90·0
Benzo-m-4-xylidide	—	89·7	92·0
Caffeine	87·5	90·8	—
Narcotine	6·3	—	—
Piperine	82·5	86·4	—
Theobromine	90·3	93·0	—

B.

Base.	$v = 4.$	$v = 8.$	$v = 16.$
Aniline	1·98	—	3·92
Dimethylaniline	0·98	1·33	1·89
Pyridine	1·99	—	3·95
Quinine	—	0·64	—
Quinoline	2·05	—	4·12
o-Toluidine	2·50	—	4·90
p-Toluidine	1·25	—	2·49
m-4-Xylidine	—	2·58	3·61

C.

Base.	$v = 32.$	$v = 40.$	$v = 64.$	$v = 80.$	$v = 160.$	$v = 240.$
m-Aminobenzoic acid	15·4	—	20·9	—	—	—
o-Aminobenzoic acid	—	54·6	—	66·3	—	—
p-Aminobenzoic acid	—	—	—	57·3	68·8	—
Diphenylamine	—	—	—	—	84·7	88·7

D.

Base.	$v = 10.$	$v = 15.$	$v = 20.$	$v = 30.$
Cinchonine	2·44	3·00	—	—
Narcotine	—	—	2·9	—
Quinidine	—	—	3·8	4·6
Quinine	0·71	—	—	—

Conclusions.—(a) The method employed is suitable for the determination of the strengths of the bases of the aromatic series and of similarly weak bases, and gives consistent results if care be taken.

(b) The method is applicable only to the more feebly basic alkaloids; for the stronger alkaloids, such as strychnine and cocaine, other methods should be adopted.

The author desires to acknowledge his indebtedness to the Principal and to the Head of the Chemical Department in permitting him to carry on this work.

THE CHEMICAL DEPARTMENT,
SOUTH-WESTERN POLYTECHNIC INSTITUTE,
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XCIII.—The Transition from Coal to Coke.

By ERIC SINKINSON.

COKE is a conductor of electricity, but it can easily be demonstrated that coal is not. It was with a view to determine whether, during the carbonisation of coal, the change from a non-conducting to a conducting condition is gradual or abrupt, that the experiments recorded in this paper were undertaken. It seems probable that the change is one in which free carbon liberated by the thermal decomposition of the coal forms an electrically conducting bridge in the non-conducting medium. Two conditions at least are necessary before this can take place: (a) that a minimum quantity of coke must be formed; (b) that the particles of free carbon forming the coke must be in a fine state of division. Consider the case where all the particles are spherical; then if in a state of maximum coarseness, where all the particles are combined into one large one, evidently there cannot be a bridge across the non-conducting medium, but if the conglomerate is finely ground, the particles will touch and form a bridge. Beyond a certain degree of fineness, the size of the particles should not affect the conductance. It seems reasonable to assume that carbon formed by heating coal will be in such a state as required by (b).

EXPERIMENTAL.

A.

Before attempting to measure the electrical resistance of carbonised coal, it was decided to find how coke itself in a fine state of division would behave when evenly distributed in a non-

conducting medium, such as pitch. Accordingly, two cokes were selected, namely, a Durham (Langley Park) and one from a Welsh bituminous coal of an upper seam in the lower coal measures. The coke was ground in a mill until it would pass a mesh of 200 to the linear inch (80 to the cm.), and dried at 105° in the ordinary way. It was then intimately mixed with 10 per cent. of pitch. The mixture was transferred to a stout cylinder of steel of 2·5 cm. cross-section, fitted with plungers top and bottom, and the whole placed in a hydraulic press, where the contents of the cylinder were subjected to a pressure of 31·5 kilos. per sq. mm. until they did not yield. In this manner, a series of briquettes was prepared with increments of 10 per cent. of pitch, until the last one reached 90 per cent.

The briquettes were prepared for the measurement of their electrical resistances in the following manner. Two holes were drilled from the top 1 cm. apart and 2 cm. deep. These were filled with mercury to establish good contact with the wires connected to the measuring instrument. This consisted of the well-known post-office box form of the Wheatstone bridge arranged with a cell and galvanometer in the circuit. A d'Arsonval mirror type of galvanometer was employed. If the resistance of the briquette was beyond the compass of the bridge, it was placed in circuit with the galvanometer and cell, and the deflexion compared with that obtained by a resistance of known magnitude. The resistances were measured in ohms, the reciprocals of which have been tabulated as conductances (mhos.) for convenience.

TABLE I.

Durham coke, per cent.	Pitch, per cent.	Resistance, ohms.	Conductance, mhos.
100	—	0·16	6·20
90	10	0·64	1·85
70	30	0·90	1·11
50	50	5·65	0·17
30	70	71·00	0·014
20	80	20,500·00	5×10^{-5}
10	90	> 500,000·00	$< 10^{-6}$
Welsh coke, per cent.			
100	—	0·20	5·0
90	10	0·75	1·33
70	30	0·87	1·15
50	50	6·40	0·15
30	70	60·00	0·016
20	80	22,000·00	$4·6 \times 10^{-5}$
10	90	> 500,000·00	$< 10^{-6}$

It is evident that more than 10 per cent. of free carbon must be present in a non-conducting medium to form an electrically conducting bridge.

B.

In order to find out what is the minimum temperature at which coal must be heated before it will conduct electricity, it was decided for experimental convenience to reverse the order and prepare a series of cokes from the same coal, carbonised every 100° below 900°, and measure the electrical resistance of each. To do this, the coal was pulverised and placed in a silica tube closed at one end to form a retort, the open end being closed by a rubber stopper carrying a delivery tube. The delivery tube was connected with an aspirator filled with a mixture of glycerol and water; a manometer was inserted to indicate the slightly diminished pressure maintained throughout carbonisation. The distillation tube and connexions were exhausted, and heat was applied by an electric muffle, the temperature of which was measured by a platinum-rhodium–platinum thermocouple. The first experiment was made at 900°, and lasted two hours.

Similar experiments were made at 800°, 700°, 600°, 500° and 400°, the last three being in glass tubes.

The cokes were removed in turn from the tubes, and powdered in a mill until they would pass a mesh of 200 to the inch (80 to the cm.). Each was briquetted at 31·5 kilos. per sq. mm., those carbonised at 900° down to 700° requiring 10 per cent. of pitch to bind them. As, however, the effect of 10 per cent. of pitch on the resistance of the coke is known from the earlier experiments, this addition can be allowed for in comparing results. The cokes carbonised below 700°, however, were self-binding under the above treatment. The briquettes were prepared for the measurement of their electrical resistance in the same way as before.

The coals employed were Durham and Welsh, and the results obtained are as follows:

TABLE II.

C.

Temperature of Durham.			Temperature of Welsh.		
Carbonisation.	Ohms.	Mhos.	Carbonisation.	Ohms.	Mhos.
900°	0·13	7·7	900²	0·20	5·0
800	0·60	1·7	800	0·75	1·3
700	100·0	0·01	700	140·00	0·006
600	4,300	2×10⁻⁴	600	6,000	1·7×10⁻⁴
550	7,900	1·2×10⁻⁴	550	40,000	2×10⁻⁵
500	>500,000	<10⁻⁶	500	>500,000	<10⁻⁶
400	>500,000	<10⁻⁶	400	>500,000	<10⁻⁶

The resistance of the briquettes became too great to measure below a carbonising temperature of 550°. By comparing the results of table I with those of II, it is evident that for a carbonising temperature of 550°, between 10 and 20 per cent. of free carbon is liberated from the coal. The critical temperature of the formation of coke lies between 500° and 550°.

In order to determine more precisely the temperature at which this change takes place, and whether the conduction commences suddenly or gradually, the method of investigation was modified in the following manner. A weighed quantity of approximately 15 grams of the dried and powdered coal under examination was introduced midway into a hard glass tube open at both ends, and in it were embedded two platinum wires 1 cm. apart, which extended beyond the open ends of the tube. The contents were held firmly in position by asbestos plugs. The tube was placed in an electric furnace, where its temperature could be raised over any desired range. The platinum wires leading from the carbonising tube were put in circuit with a battery and one of the galvanometers of the Darwin double thread recorder. A thermocouple to measure the temperature of the furnace was connected to the other galvanometer.

The purpose of this arrangement was to record simultaneously the temperature of the heated coal and the current it conducted, so that the temperature at which the coal would just conduct a current of electricity could be precisely determined. The record is registered automatically in the form of a series of dots made at intervals of a minute.

The first coal to be tried was the Welsh, used in the previous experiments. When the temperature reached 500°, the needle of the galvanometer in circuit with the coal moved from the zero position and plotted a series of ever-widening dots on the chart, thus indicating an increase in the conductance of the coal as the temperature rose above the critical value.

In this manner, critical conducting values were found for Durham, Spanish coking and non-coking coals of similar composition, a Silkstone coal, cellulose, Yacca gum resin, and starch, with the results shown in table III.

Records were also taken as the electric muffle cooled. The conductance broke down, however, on account of the contraction of mass, which consequently developed fissures.

The Spanish non-coking coal showed the lowest critical value of the series tested, namely, 450°, and the rest were from 500° to 530°. The value for cellulose was of the same order, namely, 500°.

TABLE III.

Substance.	Temperature at which conductance began.
Welsh	500°
Durham	530 }
Spanish coking	500
Spanish non-coking	450
Silkstone	500
Cellulose	500
Yacca resin	not below 640°
Starch	580°

Yacca gum resin remained non-conducting even at 640°. Although the resin appeared to have carbonised, it formed such a loose, cellular mass that no contact was set up between the ends of the platinum wires embedded in it.

Discussion of Results.

It is evident from the results of the foregoing experiments that coal under the influence of heat begins to yield free carbon at a temperature in the region of 500°. Below this temperature, decomposition has been proceeding, but not true "carbonisation" in the sense of the formation of free carbon. The critical change in the conduction at this temperature indicates that true carbonisation has begun. Since the same effect is produced with cellulose, it appears probable that the formation of free carbon at this temperature is due to the decomposition of the cellulosic constituents of the coal.

It was found by the author (this vol., p. 166) that coals carbonised about 500° gradually lost the power of producing an image on a photographic plate in the dark. It would appear that decomposition of the coal begins at 450° and continues to 500°, at which temperature sufficient free carbon has been liberated to form a conducting bridge in the coal. At this stage, there will be present not less than 10 per cent. of free carbon. It may be concluded that on carbonising coal, there is sharp transition to coke after a certain limiting temperature has been reached, evidenced by the rapid increase in its conductance above this temperature.

XCIV.—*Periodic Precipitation. Part I.   Silver Chromate in Gelatin.*

By ALEXANDER MITCHELL WILLIAMS and MARY RUSSELL MACKENZIE.

THE object of this research was to examine the influence of the different factors affecting periodic precipitation in gels. The presence of a gel would not appear to be absolutely essential for the formation of a periodic precipitate in some cases, as is shown by Dreaper (*Kolloid Zeitsch.*, 1914, **14**, 163), amongst others, but in the majority of examples studied a gel has been present. The best known case is probably that of silver chromate in gelatin, discovered by Liesegang, after whom the phenomenon is usually named, although the first investigator appears to have been Runge (Leduc, "Mechanism of Life," p. 67. See Rayleigh, *Phil. Mag.*, 1919, [vi], **38**, 738, and Bradford, *Biochem. J.*, 1920, **14**, 29). Liesegang found that the diffusion from a drop of silver nitrate solution placed on a gelatin film impregnated with potassium dichromate produced a precipitate, not continuously, but in rings — Liesegang's rings. If the reaction takes place in a test-tube, layers of precipitate are produced.

In a summary of recent work on the subject, E. Hatschek ("Second Report on Colloid Chemistry," *Rep. Brit. Assoc.*, 1919, 21) indicates the various theories advanced in explanation. The earliest, due to Ostwald, assumes supersaturation, followed by precipitation, and consequent clearing of the immediate neighbourhood of the precipitate from the reactants, so that the diffusing ion has to travel some distance before precipitation again occurs. Hatschek holds that this theory is disproved by the fact that periodic precipitation still takes place in the presence of crystalline nuclei of the precipitate or of a previous stratification which should have rendered supersaturation impossible. No allowance is here made for the slowness of a reaction in a viscous medium, and it is assumed that equilibrium exists between the crystals and the substance to be precipitated. Barger and Field (T., 1912, **101**, 1397, and private communication from Prof. Barger), however, found that a "supersaturated" solution of saponarin was colloidal, and the substance did not crystallise on addition of crystals of saponarin. Another theory, due to Bradford, attributes the removal of the reactant before the precipitate to adsorption, a view which is discussed later. Other observers have emphasised the protective action of the emulsoid present as leading to something equivalent to

"supersaturation," and it was this influence that we first sought to study.

The material employed was Cox's best gelatin. A 0·5 per cent. solution of this set readily at the ordinary temperature. Analysis showed it to yield an ash of 1·2 per cent., consisting of calcium oxide with some calcium sulphate. When dried to constant weight at 105°, the loss was 17·6 per cent. All weights of gelatin are expressed in terms of the gelatin containing 17·6 per cent. of moisture, and volume concentrations are employed throughout. The reaction first studied was the production of silver chromate by the interaction of silver nitrate and potassium chromate (for literature, see Bradford, *loc. cit.*).

The following is an example of the method employed. Five c.c. of $N/400$-silver nitrate were placed in each of a row of test-tubes, and 5 c.c. of $N/400$-potassium chromate into each of another row. Then into each test-tube were put successively 2·5, 2·6, 2·7, . . . c.c. of 0·2 per cent. gelatin. The contents of corresponding test-tubes were now mixed, and the point was noted where the precipitate of silver chromate failed to appear, say at 2·7 c.c. of gelatin. It was now easy to calculate the concentration of the silver chromate and of the gelatin. Thus the gelatin concentration is evidently

$$\frac{2 \cdot 7}{5 + 2 \cdot 7} \times 0 \cdot 2 = \frac{0 \cdot 54}{7 \cdot 7} = 0 \cdot 070 \text{ per cent.}$$

whilst the normality of the silver chromate solution is

$$0 \cdot 5 \cdot \frac{5}{5 + 2 \cdot 7} \cdot \frac{N}{100} = \frac{10N}{7 \cdot 7 \times 1600} = 0 \cdot 00081N.$$

The weight of gelatin keeping a gram-equivalent of silver chromate in solution, ignoring the saturation concentration in water $0·0002N$, is evidently

$$0 \cdot 070 \times 10 / 0 \cdot 00081 = 860 \text{ grams.}$$

It was soon found necessary to fix a maximum time for the appearance of the precipitate. This was arbitrarily selected as seventy-two hours. The test-tubes were immersed in a thermostat maintained at 25°, since leaving the solutions exposed to the ordinary temperature overnight led to discordant results. By a system of rigorous cleaning of the tubes by ammonia, hot water, and steaming, results were finally obtained reproducible within 0·2 c.c. of gelatin solution, this being the limit of accuracy attempted.

Observations were made on solutions containing up to 4·5 per cent. of gelatin. With the most concentrated solutions, precipitation usually started at the surface of the gel. This was most prob-

ably due to evaporation of water to the slightly cooler portion of
the corked tube above the surface of the water in the thermostat.
It did not seem likely from its appearance to be due merely to
adsorption concentration on the surface.   With the moderately
concentrated gels, precipitation was usually general and very fine,
although at other times it was more massive.   With the solutions
that did not set, there occurred an interval just at the limit of
precipitation, where a very small trace of precipitate settled out
and no more appeared.   This was strikingly like the separation
from a slightly supersaturated solution of the excess of solute.
With the very dilute solutions, the precipitate which appeared was
almost invariably in the form of extremely minute crystals at the
bottom of the test-tube.   Here the·slowness with which a pre-
cipitate appeared, and its minuteness when it did appear, rendered
observations somewhat difficult.   Sometimes at any concentration a
point would be found in a series of precipitates where no precipitate
had appeared on keeping, and inoculation with a trace of pre-
cipitate did not induce immediate precipitation.   Table I
exemplifies the reproducibility of the results.   Here a plus sign
indicates presence of precipitate in quantity, a plus with an interro-
gation the trace of precipitate referred to, and a minus absence
of precipitate after seventy-two hours.

TABLE I.

$N/400$-Silver nitrate and $N/400$-potassium chromate.   0·2 Per
cent. gelatin.

C.c. gel.	Precipitate.	C.c. gel.	Precipitate.	C.c. gel.	Precipitate.
1·8	+	2·4	+	2·6	+?
2·0	+	2·6	+?	2·8	+?
2·2	+	2·8	—	3·0	—
2·4	+	3·0	—	...	...
2·6	+	3·2	—	...	...
2·8	—	3·4	—	...	...

The results of a series of such observations are presented in
table II, where the first column gives the volume in litres of solution
containing a gram-equivalent of silver nitrate and potassium
chromate, and the last column the number of c.c. of gelatin solu-
tion added to 5 c.c. of the reacting solutions.   From table II may
be calculated, by the method already exemplified, the values given
in table III, where the first column contains the normality of the
silver chromate, the second the percentage concentration of the
gelatin, and the last the weight, in grams, of gelatin preventing
precipitation of a gram-equivalent of silver chromate.

TABLE II.

Volume.	Gelatin. Per cent.	C.c.
5000	0·0	0·0
1000	0·001	0·8
800	0·01	1·0
600	0·01	2·3
550	0·1	1·5
500	0·2	1·5
400	0·2	2·7
300	0·2	4·7
250	0·5	3·7
200	1·0	3·1
100	1·0	7·7
50	2·0	11·8
50	3·0	9·5
25	6·0	13·8

TABLE III.

Normality.	Gelatin. Per cent.	Gelatin. $\overline{E.W.}$
0·0002	0·0	0·0
0·00043	0·00014	3·2
0·00052	0·0017	32·0
0·00057	0·0031	55·0
0·00070	0·023	330·0
0·00077	0·046	600·0
0·00081	0·070	860·0
0·00086	0·097	1130·0
0·00115	0·20	1850·0
0·00154	0·38	2500·0
0·00197	0·61	3100·0
0·00297	1·40	4700·0
0·00345	1·96	5700·6
0·0053	4·4	830v·0

These results are presented in graphical form in Figs. 1 and 2. It will be seen from Fig. 1 that, so far as these observations extend, there is no indication of a limiting concentration of silver chromate above which gelatin will fail to prevent precipitation. Another remarkable feature is the smallness of the weight of gelatin preventing precipitation at the lowest concentration. We may compare this with the values calculated from Zsigmondy's gold numbers (Zeitsch. anal. Chem., 1902, **40**, 697) for gelatin. Thus 10 c.c. of a gold sol containing 0·055 gram per litre were protected by 0·005—0·01 milligram of gelatin, that is, 1 gram of gold required 0·01—0·02 gram of gelatin, whilst here, in a solution containing 0·08 gram of silver chromate per litre, 1 gram requires 0·02 gram of gelatin. In the case of the gold, the pro-
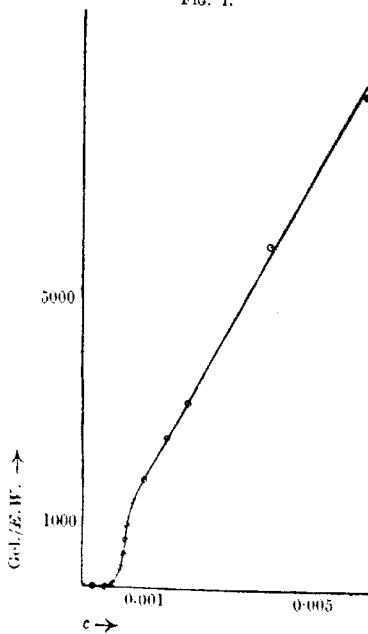
FIG. 1.

tection was exercised against 1 c.c. of 10 per cent. sodium chloride solution ($1\cdot7N$). In the case of the silver chromate, a slight excess of either reactant or of both above the concentration limits given causes precipitation. Another electrolyte is, however, present, namely, potassium nitrate, the other product of double decomposition, but addition of 10 per cent. solution of this salt ($1\cdot0N$) to any of the protected silver chromate failed to produce precipitation. From the shape of the graph in Fig. 2, dilution of any protected solution tends to in-
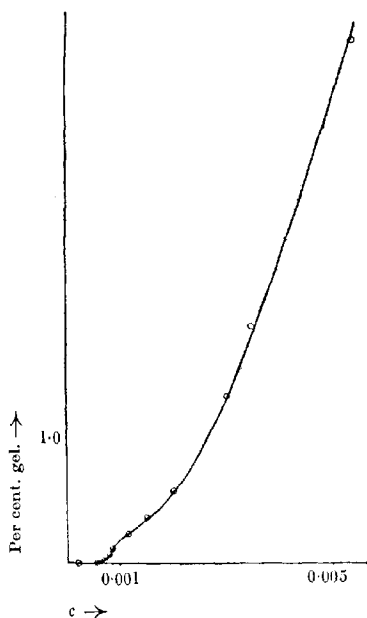
FIG. 2.

crease the protection considerably, since the curve is very concave to the y-axis, and the graph of the concentrations in the diluted solution is a straight line joining the original point to the origin.

Experiments were now made on the production of periodic precipitation in 3 per cent. gelatin. From Fig. 2 it is seen that the concentration of silver chromate may be $0\cdot0043N$ without precipitation. Actually, it was found that solutions made by diluting $N/50$-reactants to produce $0\cdot005N$-silver chromate precipitated on keeping, whilst those from $N/60$, producing $0\cdot0042N$, were stable.

Per cent. gel. $\rightarrow$

1·0

0·001   0·005

$c \rightarrow$

The initial solutions were made up by weighing, and the concentrations checked by titration. For some experiments to be described it was not desirable to have present any excess of either $Ag^{\cdot}$ or CrO_4''.

From the assumption that the " protected " silver chromate might be functioning as a colloid, it seemed reasonable to expect general precipitation to follow diffusion of either $Ag^{\cdot}$ or CrO_4'' into a gel containing the maximum amount of silver chromate. Conse-

quently, a series of tubes were half filled with 3 per cent. gelatin made $N/240$ with respect to silver chromate. The gel was allowed to set, and then solutions of silver nitrate and potassium chromate were poured above the gel. The results of a typical set of experiments are shown in tables IV and V below. It is to be noted that the earlier solutions are hypotonic to the salt solutions in the gel.

TABLE IV.

Solution above gel.	Result of diffusion beneath surface.
$N/250$-$AgNO_3$	Reddish haze 2—3 cm. below surface of gel.
$N/200$-$AgNO_3$	Intense reddish haze 1·5—2·5 below surface of gel.
$N/100$-$AgNO_3$	Traces of bands at 0·5, 1·0, 1·5.
$N/50$-$AgNO_3$	Bands at 0·2, 0·5, 0·9, 1·4, 2·1, 3·2, haze at 4·0.
$N/10$-$AgNO_3$	Fine bands 0—5·0.
$N/2$-$AgNO_3$	Thicker and closer bands 0—4·5, etc.

TABLE V.

$N/250$-K_2CrO_4	Haze 0·5—2·5.
$N/200$-K_2CrO_4	Haze 0·5—3·0.
$N/100$-K_2CrO_4	Thick band 0·5, trace at 0·9.
$N/50$-K_2CrO_4	Thick bands 0·2, 0·5, 0·8, 1·5.
$N/10$-K_2CrO_4	Thick bands 0·3, 0·6, 0·9, 1·5, 2·3.
$N/2$-K_2CrO_4	General precipitation with banded structure visible 0—1·9.

In all cases, there was a precipitate at the actual interface.

It will be seen that even under the conditions given, stratification took place. This means that in some manner or other the gel beneath a stratum of precipitate was cleared of the silver chromate. Whatever the cause, so to clear a perceptible space, diffusion must have occurred. In other words, the silver chromate did not function as a colloid with a slow rate of diffusion.

In some cases, the precipitate did not extend to the bottom of the test-tube, which was presumably due to exhaustion of the silver chromate by diffusion towards the precipitate. This was confirmed in the case of superimposed silver nitrate by the disappearance of the yellow colour from the gel. Where no stratification was recorded, hazes were sometimes noted, which were separated by clear intervals, and occasionally these hazes grew more intense in colour until a precipitate finally appeared. Where the more concentrated silver solutions were above the gels, there was frequently periodic precipitation above the surface, strata appearing for several mm. on the glass walls of the tube. In other cases, long, thin fibrils of silver chromate grew from the walls.

The next step was to find if the silver chromate diffused at all readily. Test-tubes were filled with the protected mixture as before, and the jelly was allowed to set. Above this, to a depth of 2·5 cm., was carefully poured and allowed to set some 3 per cent.

gelatin containing (a) $N/120$-potassium nitrate, (b) $N/240$-potassium nitrate, (c) no addition. In all cases, there appeared a cloudiness above the interface, which with the $N/120$-potassium nitrate advanced about $0·5$ cm., but in the other cases appeared to extend as much as $1·5$ cm. ultimately. After five days, $N/2$-silver nitrate and $N/2$-potassium chromate were poured on the top jelly. In all cases, there was precipitation at the top interface of silver chromate extending a millimetre or two downwards, and there appeared isolated portions of precipitate here and there before the second interface was reached. Precipitate did not form at the second interface, but some distance beneath, as much as $0·7$ cm. in some cases. The precipitate obtained with the silver nitrate was in all cases much greater than that obtained with the potassium chromate, which is exactly the effect to be expected from the theory of the solubility product.

It seems noteworthy that the precipitate in the upper jelly should be concentrated at the surface. In one case, where a tube broke, the top of the jelly was cut off, and, on immersion in $N/2$-potassium chromate, the precipitate formed 2 mm. beneath the cut. This almost suggests previous adsorption at the air–jelly interface of the unprecipitated silver chromate, as well as subsequent diffusion towards the precipitate. It also suggests that in some way there might be a transfer to the top surface by detachment of part of the first jelly when the second was poured in. Although unlikely, this was tested. The second jelly was cooled before pouring in, so as to set almost immediately, and a layer was allowed to set before a second supply was poured in to make up the $2·5$ cm. The effect was obtained as before. It was not obtained when the $N/2$-silver nitrate was poured on immediately, thus proving that diffusion to the new surface had not yet taken place. By reducing the depth of the top jelly, it was possible to obtain quite early precipitation in it by means of diffusing silver ion. Finally, jellies containing $N/240$-potassium nitrate were made to set in the bend of small U-tubes, and then $N/240$-silver chromate jelly set in one limb. After a week, $N/2$-silver nitrate was poured in the other limb, and a precipitate of silver chromate appeared at the surface of the jelly. There could be no chance of detachment of surface in this case.

These experiments lead to the conclusion that the silver chromate diffuses like a crystalloid. Two series of tubes were set up containing, respectively, $N/240$-silver chromate $+ N/240$-potassium nitrate and $N/240$-potassium chromate $+ N/240$-potassium nitrate, with superposed $N/240$-potassium nitrate jelly. At equal intervals $N/2$-silver nitrate was poured on the top jelly in corresponding

tubes, and the precipitates obtained were very similar, suggesting that the diffusions were comparable in the two cases. The experiments on diffusion were performed both in the thermostat and at the ordinary temperature.

It is not yet certain whether the behaviour of the silver chromate is due to some property of the gelatin itself or to the impurities in it. In the 3 per cent. gelatin employed, the concentration of $Ca^{..}$ would be $0.012N$, which is considerable. On the other hand, in the very dilute solutions earlier examined, the concentration of $Ca^{..}$ would be relatively negligible. Fig. 2 is evidently the solubility curve for silver chromate in gelatin solutions at 25°, and from it the solubility product may easily be calculated for different concentrations.

Our conclusions are that precipitation of silver chromate occurs according to the usual rules of the solubility product. By diffusion towards the precipitate, the next portion of the gel is cleared of the second ion more quickly initially than the precipitating ion can reach it in quantity, thereby setting up a concentration gradient, so that this ion must travel some distance before further precipitation takes place. It is obvious that the gel incidentally provides mechanical support for the precipitate.

The distance at which a second stratum appears is evidently dependent on the relative rates of diffusion of the precipitating ion, say, $Ag^{.}$ and of the $CrO^{''}$. The diffusion of the first ion may be hindered by the precipitate or by precipitation at the precipitate. The faster the second ion diffuses to the precipitate, the further from the precipitate will be the mean value of the concentration in the region of diffusion, and hence, under suitable conditions (that is, not too high concentration of one reactant, for example, potassium chromate, behind the precipitate), the further from the precipitate will be the place at which new precipitate forms. Diffusion is a very slow process, and in the case considered can only be accelerated by reducing the concentration to which diffusion proceeds, that is, the concentration at the precipitate. Bradford assumes this reduction is accomplished by adsorption, but although adsorption at the surface of the adsorbent is faster than diffusion, it cannot accelerate diffusion otherwise than is here indicated, and since simple continuous precipitation at the stratum could have the same effect, it is unnecessary at present to assume adsorption.

Summary.

(1) Observations have been made on the variation of the solubility of silver chromate with gelatin-concentration in aqueous solution at 25°.

(2) It is shown that the silver chromate does not behave as a protected colloid, but as a crystalloid, and that its precipitation follows the usual rules of the solubility product.

CHEMISTRY DEPARTMENT,
UNIVERSITY, EDINBURGH. [*Received, May 20th, 1920.*]

XCV.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part II. The Dinitrotoluenes.*

By JAMES KENNER and MICHAEL PARKIN.

A REVIEW of the results obtained by previous workers on the reactivity of substituents in the benzene nucleus, as determined by the presence of nitro-groups in the ortho- or para-position led one of us (Kenner, T., 1914, **105**, 2717) to associate this influence with the meta-directive properties of this group, and it was suggested that ortho-para-directive groupings or atoms might confer mobility on substituents in the meta-position. Further, it was concluded that the displacement of such mobile substituents depended primarily on the formation of a molecular compound, which underwent rearrangement and decomposition, leading to the products actually isolated. In this way, the failure of the nitro-group to exert its usual steric effects was accounted for, but the action of such influences, for example, on the part of methyl groups in inhibiting the formation of the necessary additive compound furnished a simple explanation of some exceptional cases which previously seemed inexplicable.

With the object of testing the validity of these conclusions, a qualitative study of the action of ammonia and sodium methoxide on 2:3-, 3:4-, and 2:5-dinitrotoluenes has been made.

Of the two nitro-groups in 2:3-dinitrotoluene, it is clear from the foregoing that the effect of the methyl group would be expected to make that in the 3-position the more mobile. A necessary preliminary of its displacement, however, is the formation of an additive compound with the 2-nitro-group, but this is sterically inhibited by the methyl and the 3-nitro-groups. As a result, the 3-nitro-group must take part in the preliminary reaction, and the 2-nitro-group be displaced. Experiment fully confirmed this inference, the respective products of the action of sodium methoxide

and of methyl-alcoholic ammonia being easily identified as pure 6-nitro-*o*-tolyl methyl ether and 3-nitro-*o*-toluidine.

The case of 3 : 4-dinitrotoluene is simpler, since the two nitro-groups are equally accessible for the purpose of the formation of the preliminary molecular compound.   The influence of the methyl group again favours the displacement of the 3-nitro-group, and, indeed, the product of the action of methyl-alcoholic ammonia at 150° was found to consist to the extent of 93·5 per cent. of 4-nitro-*m*-toluidine, the remainder being in all likelihood 3-nitro-*p*-toluidine.   The main product of the action of sodium methoxide was an insoluble compound, evidently of high molecular weight, and very probably a stilbene derivative of the type prepared by Green (T., 1908, **93**, 1721) from *p*-nitrotoluene.   A small amount of 6-nitro-*m*-tolyl methyl ether was obtained; the oily portion of this product, which did not crystallise, may possibly have contained 2-nitro-*p*-tolyl methyl ether, since this compound is described as melting at 8·5° (de Vries, *Rec. trav. chim.*, 1909, **28**, 2), but the quantity available was too small for identification.

The results obtained with 2 : 5-dinitrotoluene show that in this case both the possible isomerides are produced.   Whilst the 5-nitro-group may be expected to be the more mobile, it is not surprising that the steric influence of the methyl group above referred to asserts itself and sufficiently reduces the velocity of formation of the additive compound with the 2-nitro-group to permit of the 5-nitro-group taking an appreciable part in the preliminary reaction.   When, therefore, 2 : 5-dinitrotoluene was heated with methyl-alcoholic ammonia at 160° for six hours, a period which sufficed for the completion of the reaction in the case of the 3 : 4-isomeride, about 45 per cent. of the dinitro-compound remained unchanged.   By prolonging the reaction, a mixture of amines was produced, consisting of about 88 per cent. of 5-nitro-*o*-toluidine with 12 per cent. of 6-nitro-*m*-toluidine.   On the other hand, the relatively small quantity of crystals which separated from the oily product of the action of sodium methoxide on the dinitrotoluene consisted of 4-nitro-*m*-tolyl methyl ether.   Apparently, therefore, the influence of the methyl group is not sufficiently great completely to prevent the formation of the alternatively possible products.

The colour changes, indicative of the formation of an additive compound, which take place on adding ammonia to the three dinitrotoluenes are in accord with the explanations given above. 3 : 4-Dinitrotoluene at once gives a red coloration in the cold, the 2 : 5-compound gives a red colour only on warming, and the 2 : 3-compound gives only a yellow colour, even when the mixture is heated.

K K 2

The experimental results are therefore easily explained in terms of the hypothesis previously advanced. This is also very largely true of the interesting data communicated by Holleman and his collaborators (*Rec. trav. chim.*, 1915, **35**, 1), and summarised below in regard to the dichloronitrobenzenes and the chlorodinitrobenzenes. In the table, the figures in clarendon type indicate the substituents which suffer displacement under the influence of sodium methoxide, diethylamine, or ammonia:

	Reaction constants at 85° (time in hours).			Reaction constants at 25° (time in hours).	
$NO_2:Cl:Cl$.	CH_3ONa.	$(C_2H_5)_2NH$.	$Cl:NO_2:NO_2$.	CH_3ONa.	NH_3.
1:2:4	19·41	0·027	**1:2:4**	90·6	0·0206
1:3:4	17·42	0·0044	**1:2:5**	33·5	0·00512
1:2:5	3·93	0·0067	**1:3:4**	26·22	0·00807
1:2:3	1·74	0·0016	**1:2:3**	6·0	0·0137
1:2:6	0·135	0·00024	**1:2:6**	2·76	0·0121

Considering first the results from the dichloronitrobenzenes, the displacement of the chlorine atom in the ortho-position with respect to the nitro-group in the 1:2:4-compound in preference to that in the para-position is particularly interesting. It is in accordance with the views now represented, but the fact that the reaction constant of *p*-chloronitrobenzene is greater than that of the ortho-compound led Holleman to expect that the para-atom would be displaced. It will be observed that the order of the constants observed with diethylamine differs slightly from those obtained with sodium methoxide, showing that the nature of the reagent cannot be neglected in considering the relative activities of such compounds. The order of the values obtained with sodium methoxide corresponds with that to be anticipated as a result of applying the considerations already discussed. Both the nitro-group and the second chlorine atom co-operate in rendering one of the chlorine atoms of the 1:2:4-isomeride mobile; in the 1:3:4-derivative, the influence of the 3-chlorine atom is contrary to that of the nitro-group, but there is no steric hindrance to the formation of the additive compound such as may very possibly occur in the case of the otherwise similar 1:2:5-derivative; in the 1:2:3-compound there is the added complication of steric hindrance by the chlorine atom in the 3-position to the later stages of the reaction, whilst the relative stability of the 1:2:6-isomeride is accounted for by the powerful steric hindrance to the formation of the initial compound.

The chlorodinitrobenzenes are more interesting, since all three substituents are capable of displacement. Apparently, only one product is obtained in each case, and the result of displacement is

in every case in accord with anticipation, except that in the case of the $1:2:5$-compound it is not possible to foresee which of the opposing influences discussed in connexion with $2:5$-dinitrotoluene will be the stronger. The great divergence between the order of the values of the two sets of reaction constants suggests that in one or both series the nature of the nitro-derivative is not the chief determining factor in determining their relative activities, and little value can attach to their discussion from this point of view. Of the two series, the values obtained with sodium methoxide correspond the better with the views expressed above. A prominent feature of the quantitative results is the great increase in the magnitude of the constants over those of the corresponding dichloronitrobenzenes. Holleman illustrates this by a comparison of $2:4$-dichloronitrobenzene with 4-chloro-o-dinitrobenzene $(1:3:4)$, of $3:4$-dichloronitrobenzene with 2-chloro-p-dinitrobenzene $(1:2:5)$, and of $2:3$-dichloronitrobenzene with 3-chloro-o-dinitrobenzene $(1:2:3)$. Of each pair, the first suffers displacement of a chlorine atom, the second of a nitro-group in molecules otherwise identical, but the ratios of the respective constants at $25°$ are 800, 1000, and 2000. Similarly, the chlorodinitrobenzenes react with methyl-alcoholic ammonia at $100°$, but the dinitrotoluenes were recovered practically unchanged after treatment under such conditions.

As regards the constitution of the intermediate compounds postulated in these reactions, arguments were advanced in the previous paper against the quinonoid formula (I), proposed by several workers, and preference was given to Werner's (II) or, alternatively, to Pfeiffer's formula (III):

(I.)   (II.)   (III.)

The results since obtained would appear to strengthen the case against the quinonoid formula, which can offer no satisfactory explanation of the formation of one of the possible isomerides, either alone or in an overwhelmingly predominating amount. For example, in order to explain on this basis the formation of 3-nitro-o-toluidine from $2:3$-dinitrotoluene, it appears necessary to assume that the methyl group exerts some directive influence, resulting in the formation of the compound (IV). In the case of $3:4$-dinitrotoluene, however, such an influence would be expected to involve the formation of the product (V), from which 3-nitro-p-toluidine should be obtained.

Considerations of this kind appear to lead inevitably to the choice of some formula of the type (II) or (III).

(IV.)   (V.)

EXPERIMENTAL.

The dinitrotoluenes were prepared according to the directions of Meisenheimer and Hesse (*Ber.*, 1919, **52**, 1161), whilst the strengths of sodium methoxide and ammonia solutions were those employed by Holleman (*loc. cit.*), in order that the results obtained in the two series of experiments might be comparable.

Action of Sodium Methoxide on 2:3-*Dinitrotoluene.*—2:3-Dinitrotoluene (1·5 grams) was heated for nine hours on the water-bath with a solution of sodium (0·2 gram) in methyl alcohol (5 c.c.). The product consisted of a dark oil, which distilled almost entirely at 140°/24 mm., leaving a small, tarry residue. There can be no doubt that the product was 6-nitro-*o*-tolyl methyl ether, since this compound, which is referred to by Hofmann and Miller (*Ber.*, 1881, **14**, 568) as a yellow liquid, was obtained as a golden-yellow oil (b. p. 134°/21 mm.) by the action of sodium methoxide on 2-chloro-3-nitrotoluene (Found : N = 8·53. Calc.: N = 8·38 per cent.).

2 : 2′-*Dimethoxy*-3 : 3′-*azoxytoluene,*
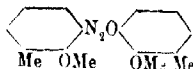
which was also produced in small amount in the above preparation, separated from alcohol in diamond-shaped prisms melting at 144° (Found : N = 9·86. $C_{16}H_{18}O_3N_2$ requires N = 9·79 per cent.).

Action of Ammonia on 2:3-*Dinitrotoluene.*—The dinitro-compound was quite unaffected by treatment on the water-bath with 2·5N-methyl-alcoholic ammonia (20 c.c.). The mixture was therefore heated under pressure for fifteen hours at 150 –160°. The resulting solution, on evaporation, left a residue (m. p. 97°), which did not depress the melting point of 3-nitro-*o*-toluidine.

Reduction of 2 : 3-*Dinitrotoluene.*—2-Nitro-*m*-toluidine was obtained by Limpricht (*Ber.*, 1885, **18**, 1452) by reducing 2:3-dinitrotoluene with hydrogen sulphide in boiling alcoholic ammonia solution. As it was a possible product of the above reaction, it was decided to attempt its preparation.

(1) In an experiment by Mr. H. Burton, hydrogen sulphide was passed for three hours through a boiling solution of the dinitro-compound (3·6 grams) in alcohol (25 c.c.) to which ammonia solution (10 c.c. : D 0·880) had been added. The product obtained after filtration and evaporation was fractionally crystallised from alcohol. The main product, after recrystallisation from benzene, consisted of yellow prisms melting at 150°. Analysis showed it to be *dinitroditolyl sulphide*, $(C_6H_3Me\cdot NO_2)_2S$, most probably the 2 : 2′ : 6 : 6′-isomeride (Found : $N = 8·92$. $C_{14}H_{12}O_4N_2S$ requires $N = 9·2$ per cent.). The more readily soluble product, after recrystallisation from benzene, melted at 54°. Although Limpricht's base melted at 55°, it is uncertain whether our compound was 2-nitro-*m*-toluidine, since it was not acetylated under ordinary conditions. The quantity available was too small for analysis, and the course of the present work did not necessitate closer investigation.

(2) A solution of stannous chloride (11·4 grams) and hydrogen chloride (16 grams) in absolute alcohol (50 c.c.) was added drop by drop to a cold solution of 2 : 3-dinitrotoluene (3·64 grams) in alcohol (50 c.c.). After half an hour, the solution was diluted and extracted with ether. The residue, after evaporation of the ether, was resolved into its components by treatment with light petroleum. The more readily soluble consisted of unchanged dinitro-compound, whilst the sparingly soluble product (1·2 grams) separated from a mixture of ether and light petroleum in long, stout, deep red prisms melting at 106° (Found : $N = 18·45$. $C_{14}H_{13}O_4N_4$ requires $N = 18·66$ per cent.). The compound was therefore a *dinitroazotoluene*, probably the 2 : 2′ : 3 : 3′- rather than the 6 : 6′ : 2 : 2′-isomeride.

Action of Sodium Methoxide on 3 : 4-*Dinitrotoluene.*— The products obtained from 3 : 4-dinitrotoluene (3 grams) consisted of a black, insoluble product (0·8 gram), probably a stilbene derivative (see p. 853), a dark red, resinous product (0·5 gram) soluble in alkali, and an oil. From the latter, a few crystals separated after some weeks. These, after purification by draining on a porous tile and solution in light petroleum, were obtained as colourless plates melting at 53–57°. A mixture with an equal amount of the original dinitrotoluene (m. p. 59–60°) softened at 40° and melted completely at 50°. The quantity available was too small for analysis, but there can be little doubt that the substance was 6-nitro-*m*-tolyl methyl ether, the description of which corresponds with our product, and of which the melting point is variously given as 51–52° (Reissert and Scherk, *Ber.*, 1898, **31**, 398), 60° (Fischer and Rigaud, *Ber.*, 1902, **35**, 1259), and 62° (Khotinsky

and Jacopson-Jacopmann, *Ber.*, 1909, **42**, 3099). 2-Nitro-*p*-tolyl methyl ether forms pale yellow crystals melting at 8·5° (de Vries, *loc. cit.*), and it is therefore possible that some of this was present in the portion of the oil which did not solidify.

Action of Ammonia on 3:4-*Dinitrotoluene.*—From the product obtained by heating 3:4-dinitrotoluene (1·82 grams) with 2·5*N*-methyl-alcoholic ammonia (32 c.c.) for six hours at 150° were obtained pure 4-nitro-*m*-toluidine (m. p. 109°; 1·1 grams), and a further quantity (0·15 gram) of impure product (m. p. 82°). By the application of Holleman's freezing-point method, it was shown that this corresponded with mixtures containing 4-nitro-*m*-toluidine with either 32 or 61 per cent. of 3-nitro-*p*-toluidine. Since the addition of the latter base to our product caused a rise in the temperature of solidification in agreement with the calculated, it contained 61 per cent. of this base.

4-*Nitro-o-tolyl Methyl Ether.*—The product of the interaction of 2-chloro-5-nitrotoluene and sodium methoxide, after isolation in the usual manner, crystallised from light petroleum in long, radiate needles melting at 63° (Found : N = 8·35. $C_8H_9O_3N$ requires N = 8·38 per cent.).

Action of Sodium Methoxide on 2:5-*Dinitrotoluene.*—By the action of sodium methoxide on 2:5-dinitrotoluene (3 grams). an oil (2 grams) was obtained, from which a quantity of crystals separated overnight; a further quantity separated when the oil was stirred with light petroleum. These, when collected and purified by crystallisation from light petroleum, melted at 55°, the melting point of 4-nitro-*m*-tolyl methyl ether (Reissert and Scherk, *loc. cit.*). A mixture with the original dinitro-derivative liquefied at the ordinary temperature, whilst that with 4-nitro-*o*-tolyl methyl ether melted at 28°. It is therefore clear that one of the products of the reaction was 4-nitro-*m*-tolyl methyl ether, but the other possible isomeride may also have been present, since the oil did not solidify completely even after some months.

6-*Nitro*-m-*toluidine.*—This compound was prepared according to the directions of Noelting and Stoecklin (*Ber.*, 1891, **24**, 564), who recommend steam-distillation of the products of nitrating *m*-toluidine until the distillate is no longer yellow. It was, however, found that 6-nitro-*m*-toluidine is slightly volatile in steam, and therefore the yellow colour does not completely disappear. When 16 litres of distillate, containing 11·7 grams of base, had been collected from the product of nitrating 32 grams of *m*-toluidine, the melting point of the crystals deposited, which had gradually risen during the distillation from 63° to 87°, suddenly rose to 133°, which was also the melting point of the residue in the distillation

flask. Although the authors named give 138° as the melting point, this could not be attained in the present case, either by repeated crystallisation or by purification of the base through its acetyl derivative, which was easily obtained by the addition of a drop of sulphuric acid to a mixture of the base with acetic anhydride. It separated from dilute alcohol in small prisms (m. p. 104°), and was easily hydrolysed by treatment with concentrated hydrochloric acid (Found: $N = 14.20$. Calc.: $N = 14.4$ per cent.).

2-Nitro-5-nitrosotoluene.—6-Nitro-*m*-toluidine (10 grams) was shaken for sixteen hours with Caro's acid (400 c.c.) from potassium persulphate (70 grams) and sulphuric acid (77 grams). The product (7 grams), after crystallisation from alcohol, melted at 113° (Found: $C = 50.37$; $H = 3.59$. $C_7H_6O_3N_2$ requires $C = 50.60$; $H = 3.61$ per cent.).

By oxidation with fuming nitric acid (10 parts), it was easily converted into $2:5$-dinitrotoluene.

Action of Ammonia on $2:5$-Dinitrotoluene.—The dinitro-compound (1 gram) was heated with alcoholic ammonia (32 c.c.) at 150° for fifteen hours. The residue obtained by evaporating the resulting solution was stirred with cold concentrated hydrochloric acid. The base precipitated from the acid solution by ammonia melted at 115—120°, but after crystallisation from dilute alcohol it melted at 127°, as did also its mixture with 5-nitro-*o*-toluidine. Since, on the other hand, its mixture with 6-nitro-*m*-toluidine melted at 114—115°, it is clear that the product in question was 5-nitro-*o*-toluidine. The low yield was due to the formation of a tarry product, which was insoluble in hydrochloric acid, and was not further investigated. According to measurements of the solidification points of mixtures of 5-nitro-*o*-toluidine with 6-nitro-*m*-toluidine, the crude base precipitated from acid solution contained about 88 per cent. of the former.

THE UNIVERSITY,
SHEFFIELD.

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XCVI.—*Complex Metallic Ammines.   Part III.*
Dichlorotetrapyridinecobalt Salts.

By Thomas Slater Price.

In a previous communication (Price and Brazier, T., 1915, **107**, 1913), it has been shown that *trans*-dichlorodiethylenediamine-cobalt salts give rise to peculiar additive compounds with certain organic dibasic acids.   Evidence was obtained that this peculiarity is also shown by the *trans*-dibromodiethylenediaminecobalt salts. It is characteristic of these two series of salts that the chloride or bromide from which they are derived forms additive compounds with the respective halogen hydracids, namely,

$$1:6[Cl_2Co\ en_2]Cl,HCl,2H_2O$$
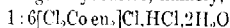
and $1:6[Br_2Co\ en_2]Br,HBr,2H_2O$.   Dichlorotetrapyridinecobalt chloride and *trans*-dichlorotetramminecobalt chloride do not, how-ever, form additive compounds with the halogen hydracids, their respective formulæ being $[Cl_2CoPy_4]Cl,6H_2O$ and

$$[Cl_2Co(NH_3)_4]Cl,H_2O,$$

and it was therefore of interest to see if the formation of additive compounds took place when their salts with dibasic organic acids were prepared.   The dichlorotetrapyridinecobalt salts were chosen for examination, since they are fairly stable in aqueous solution (Werner and Feenstra, *Ber.*, 1906, **39**, 1538), whereas the dichloro-tetramminecobalt salts rapidly change to chloroaquo- and diaquo-tetrammine compounds.   Werner and Feenstra (*loc. cit.*) prepared dichlorotetrapyridinecobalt chloride by the action of chlorine on an aqueous solution containing cobalt chloride and pyridine.   It being somewhat difficult, according to this method, to regulate the amount of chlorine entering into reaction, it was decided to generate the chlorine electrolytically in the presence of the solution of cobalt chloride containing pyridine, the necessary chlorine being provided by the addition of sodium chloride to the electrolyte.   A divided cell was used, and the preparation was completely successful,* better yields of dichlorotetrapyridinecobalt chloride being obtained than by Werner and Feenstra's method.

The chloride thus prepared had the appearance described by Werner and Feenstra, and gave the correct analytical results, but

* When pyridine is replaced by ethylenediamine a mixture of dichloro-diethylenediaminecobalt chloride and triethylenediaminecobalt chloride appears to be formed.   With diethylamine in place of pyridine an insoluble, amorphous green complex cobalt compound is produced, the composition of which seems to be variable and has not yet been elucidated.

when various tests were applied to its aqueous solution, some discrepancies were noticed. For example, Werner and Feenstra state that a 5 per cent. solution gives no precipitate with mercuric chloride, cobalt nitrate, or ferric chloride. With the specimen prepared electrolytically, however, a 5 per cent. solution could not be obtained at the ordinary temperature, but only an approximately 1 per cent. solution; this gave precipitates immediately with mercuric chloride, cobalt nitrate, and ferric chloride. In order to find an explanation of these discrepancies, a sample of the chloride was prepared according to Werner and Feenstra's method. It was found to give exactly the same reactions and have about the same solubility as the salt prepared electrolytically, so that the statements made by Werner and Feenstra are evidently in error.

In order to make certain that the chloride had been correctly characterised, other salts were prepared and analysed; these consisted of the nitrate (previously obtained by Werner and Feenstra), dithionate, benzylthiosulphate, and tetranitrodiamminecobaltate. In agreement with Werner and Feenstra, the thiocyanate and iodide could not be obtained.

One great difficulty experienced in the preparation of these salts has been to obtain them in the air-dry condition. When definitely crystalline, they separate in shining spangles, which felt together when collected, and the mass does not dry readily on a porous tile. The simpler salts are, as it happens, readily soluble in alcohol, and if the collected crystals, after being washed with water, are washed with a little alcohol and then with ether,* they no longer felt together. Even then, however, during the abnormally damp weather which has prevailed during the time this investigation has been in progress, it has been impossible to be quite certain that the salts were air-dry, so that estimations of the water of crystallisation were likely to give fictitious values. The nitrate was always found to contain more than the one molecule of water of crystallisation given by Werner and Feenstra; this difference may possibly be accounted for by the difference in the amount of moisture normally present in the air at Birmingham and Zürich, since Price and Brazier found similar discrepancies in the water of crystallisation of oxalatodiethylenediaminecobalt bromide and chloride (T., 1915, 107, 1376, 1727).

In agreement with the fact that dichlorotetrapyridinecobalt chloride does not form an additive compound with hydrogen chloride, additive compounds with organic dibasic acids (oxalic, malonic, and thiodiacetic acids) were not obtained.

* Except where otherwise stated, this method of washing was always used.

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EXPERIMENTAL.

Electrolytic Preparation of Dichlorotetrapyridinecobalt Chloride,
$[Cl_2CoPy_4]Cl,6H_2O.$

The divided cell used consisted of a central anode compartment
made from a glass cylinder with parchment paper tied over the
lower end. This stood on a glass triangle in a beaker containing
the catholyte and a platinum foil cathode. A rotating platinum
electrode, similar to that described in Perkin's "Practical Methods
of Electrochemistry," p. 198, was used as anode. The catholyte
was a 5 per cent. solution of sodium chloride, to which sufficient
hydrochloric acid was added from time to time during the electro-
lysis to keep it acid. The anolyte was prepared as follows:
20 grams of cobalt chloride hexahydrate and 5 grams of sodium
chloride were dissolved in 60 c.c. of hot water; after cooling, the
solution was placed in the anode compartment, and the anode
started rotating. Thirty grams (31·5 c.c.) of pyridine were then
added, and the current immediately switched on, the current
density being 2 amperes per sq. dm. and current strength 1 ampere.
Owing to the formation of complex ions, there was very little
migration of cobalt ions to the catholyte, the simpler ions carry-
ing most of the current. As electrolysis proceeded, the anolyte
became darker and darker in colour, finally being very dark brown,
and a sludge of green crystals formed. No cooling was necessary.
The current was passed for the time theoretically necessary to give
one atom of chlorine for each atom of cobalt taken (1 ampere for
3·4 hours), and then the contents of the anode compartment were
poured into a beaker and allowed to remain overnight. The
collected and washed crystals were dried on a porous tile. The
yields obtained in three different experiments were 14·5, 13·8, and
14·8 grams respectively, the product being completely soluble in
water.

When prepared according to Werner and Feenstra's method
(*loc. cit.*), the same quantities of cobalt chloride and pyridine were
taken, but only 30 c.c. of water. These authors state that a deep
blue solution results when the pyridine is added to the cobalt
chloride solution, but this is not the author's experience, a pink
precipitate always forming. The yield of crude chloride obtained
was 9·5 grams (Werner and Feenstra give 10 grams); the salt was
contaminated with a small quantity of a pale green, insoluble
compound, and was thus far from pure.

The purity of the electrolytic preparation may be gauged from
the fact that, without recrystallisation, it gave Co = 10·06, whereas

$C_{20}H_{20}N_4Cl_3Co,6H_2O$ requires $Co = 10·00$ per cent. One recrystal-
lisation from water at 50—60°, containing a little hydrochloric
acid, gave the analytically pure substance.

The nitrate, $[Cl_2CoPy_4]NO_3,xH_2O$, was readily obtained accord-
ing to Werner and Feenstra's method, the crystals being plates
rather than needles. It seemed impossible to obtain the salt in
an air-dry condition; when dehydrated over phosphoric oxide in a
vacuum desiccator,* one sample which, after recrystallisation, had
been dried in the air for ten days, gave $H_2O = 14·02$, whilst a
second sample, after being dried for two days only, gave
$H_2O = 13·15$ per cent. For four molecules of water of crystallisa-
tion the loss should be 12·42, and for five molecules 15·06, per cent.
The second sample gave $Co = 9·95$, whereas $C_{20}H_{26}O_5N_5Cl_2Co,4H_2O$
requires $Co = 10·16$ per cent. The dehydrated first sample gave
$Co = 11·71$, $Cl = 14·03$, $C_{20}H_{20}O_3N_5Cl_2Co$ requiring $Co = 11·61$,
$Cl = 13·95$ per cent.

Dichlorotetrapyridinecobalt dithionate, $[Cl_2CoPy_4]_2S_2O_6,xH_2O$,
was precipitated almost quantitatively as a green, microcrystalline
powder when a solution of 2 grams of sodium dithionate in 20 c.c.
of water was added to a solution (at 50°) of 1 gram of the dichloro-
chloride in 50 c.c. of water containing a little hydrochloric acid.
After drying in the air for three days, the salt lost 17·00 per cent.
of water in a desiccator over phosphoric oxide, whereas after air-
drying for thirty days it lost 14·57 per cent.

$$C_{40}H_{40}O_6N_8Cl_4S_2Co_2,xH_2O$$
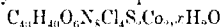
requires $H_2O = 17·04$ for $x = 12$. and $H_2O = 14·62$ per cent. for
$x = 10$. The dehydrated salt gave (Found : $Co = 11·08$; $Cl = 13·27$.
$C_{40}H_{40}O_6N_8Cl_4S_2Co_2$ requires $Co = 11·21$; $Cl = 13·48$ per cent.).

The *double* salt of dichlorotetrapyridinecobalt chloride with
mercuric chloride, $2[Cl_2CoPy_4]Cl.3HgCl_2$, was obtained as an in-
soluble, pale green, (?) microcrystalline precipitate when 50 c.c. of
a 2 per cent. solution of the dichloro-chloride were mixed with
50 c.c. of a 2 per cent. solution of mercuric chloride, both solutions
being at 50°. After cooling, the precipitate was collected, well
washed with water, and dried in the air for three days (Found :
$Co = 6·64$; $Hg = 33·47$. $C_{40}H_{44}N_8Cl_6Co_2.3HgCl_2$ requires $Co = 6·63$;
$Hg = 33·76$ per cent.).

To prepare *dichlorotetrapyridinecobalt tetranitrodiammine-
cobaltate*, $[Cl_2CoPy_4](NO_2)_4Co(NH_3)_2],xH_2O$, 1 gram of the
dichloro-chloride dissolved in 70 c.c. of water was mixed with
1 gram of potassium tetranitrodiamminecobaltate dissolved in

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* No loss of pyridine occurred. When such loss did take place it was
immediately detected by the odour. These salts could not be dehydrated
by heating, as pyridine was then driven off.

50 c.c. of water, both solutions being at 50°.   The desired salt immediately separated (practically quantitatively) as a micro-crystalline, pale yellowish-green precipitate.   After being dried in the air for three days, it lost 3·19 per cent. of water in a desiccator over phosphoric oxide, whereas after air-drying for thirty days it lost 2·83 per cent. $C_{20}H_{26}O_8N_{10}Cl_2Co_2,xH_2O$ requires 2·43 per cent. for $x=1$ and 4·74 per cent. for $x=2$.   (Anhydrous substance: Found: Co = 16·40; Cl = 9·68; N = 19·16.

$$C_{20}H_{26}O_8N_{10}Cl_2Co_2$$

requires Co = 16·31; Cl = 9·80; N = 19·37 per cent.)

Dichlorotetrapyridinecobalt benzylthiosulphate,

$$[Cl_2CoPy_4]S_2O_3 \cdot C_7H_7.$$
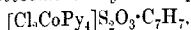
is readily obtained in quantitative yield by mixing solutions of the dichloro-chloride (1·5 grams in 70 c.c. of water at 50°) and sodium benzylthiosulphate (1·5 grams in 30 c.c. of water).   It is practically insoluble in water, and separates as a pale green, microcrystalline precipitate (Found: Co = 9·14; N = 8·45. $C_{27}H_{27}O_3N_4Cl_2S_2Co$ requires Co = 9·08; N = 8·63 per cent.).

The dichlorotetrapyridinecobalt salts of dibasic organic acids seem to be much more readily soluble in water than the chloride, with the result that the latter usually crystallises from solution when an attempt is made to prepare the organic salt.   For example, 1·5 grams of the dichloro-chloride were readily soluble in 10 c.c. of water at 50° in the presence of 1·5 grams of thiodiacetic acid; on cooling, however, practically pure hydrated dichloro-chloride separated   (Found: Co = 9·96;   Cl = 17·84.   Calc.:   Co = 10·00; Cl = 18·04 per cent.).   After dehydration over phosphoric oxide it gave Co = 12·32, the theoretical percentage being 12·24.   On the addition of solid sodium carbonate to the filtrate, a small quantity of a green precipitate was further obtained, which possibly consisted of the thiodiacetate, but when placed on a porous tile it lost pyridine and turned blue.   Similarly, the hydrated dichloro-chloride separated when malonic acid was used, although in not quite as pure a condition as with thiodiacetic acid.

Attempts to prepare the oxalate did not give a pure product, although from different preparations salts giving the same analytical results were obtained.   Thus, in one preparation, 1·5 grams of the dichloro-chloride and 2 grams of oxalic acid were dissolved in 60 c.c. of water at 50°, and the solution was cooled.   Pale green crystals (microscopic plates) separated, which lost pyridine in a desiccator over phosphoric oxide, the residue turning blue (Found in air-dried sample: Co = 9·65, 9·72; Cl = 13·11 per cent.).   In another preparation, the dichloro-chloride (1·5 grams) was dissolved in 40 c.c. of water at 50°, and then mixed with the oxalic acid

(2 grams) dissolved in 10 c.c. of water at 50°. The resulting salt gave $Co = 9.62$; $Cl = 13.02$ per cent. These analyses give the atomic proportion of cobalt to chlorine as $4 : 9$, which is satisfied by the formula $3\{[Cl_2CoPy_4]C_2O_4H,4H_2O\},[Cl_2CoPy_4]Cl,6H_2O$, requiring $Co = 9.78$; $Cl = 13.23$ per cent. The salt could not be recrystallised without decomposition. Trituration with a saturated solution of oxalic acid did not lead to the isolation of a pure product. Other methods of preparation were not investigated, since there was no object in pursuing the matter further.

CHEMICAL DEPARTMENT,
MUNICIPAL TECHNICAL SCHOOL,
BIRMINGHAM.

XCVII.—*Arsinic Acids Derived from Guaiacol and Veratrole. Constitution of the Polyarsenides.*

By ROBERT GEORGE FARGHER.

THE literature of the organic compounds of arsenic contains no account of the arsinic acids derived from guaiacol and veratrole, though the conversion of *p*-hydroxyphenylarsinic acid into a dihydroxy-acid, presumably $3 : 4$-dihydroxyphenylarsinic acid, by means of potassium persulphate has been claimed (D.R.-P. 271892). Trial of this reaction showed that the yield was poor and the product a mixture of $3 : 4$-dihydroxyphenylarsinic acid with the unchanged acid. These were separable with difficulty, and their identity was most readily established by complete methylation and fractional crystallisation of the product.

3-Amino-4-hydroxyphenylarsinic acid and *3-amino-4-methoxyphenylarsinic acid* presented an alternative source, but the energetic treatment required to effect the decomposition of their diazo-compounds (compare D.R.-P. 95339; *J. Soc. Chem. Ind.,* 1898, **17**, 314; P., 1905, **21**, 206; French Pats., 167211, 228539) resulted in the almost entire destruction of the arsenical complex. The Bucherer reaction (compare *Ber.,* 1917, **50**, 101, where earlier references are given) also proved to be inapplicable.

The reaction devised by Bart (D.R.-P. 250264, 254092, 254345) therefore presented the most satisfactory method of obtaining the required substances. The preparation of the necessary amines was facilitated by the appearance of a communication by Cardwell and

Robinson (T., 1915, **107**, 257) dealing with 4- and 5-nitroguaiacol and 4-nitroveratrole.

These were reduced to the corresponding amines, which were diazotised and combined with sodium arsenite in alkaline solution, giving rise to 3-*hydroxy-4-methoxyphenylarsinic acid*, 4-*hydroxy-3-methoxyphenylarsinic acid*, and 3 : 4-*dimethoxyphenylarsinic acid* respectively.

All three acids were readily converted into the corresponding nitro-acids, and the reduction of these was investigated.

On complete reduction with sodium hyposulphite, only 5-*nitro*-4-*hydroxy-3-methoxyphenylarsinic acid* was found to undergo the normal reduction to the *arsenobenzene*. 5-*Nitro-3-hydroxy-4-methoxyphenylarsinic acid* yielded a product containing twice as much arsenic as required by the arsenobenzene formula, whilst 5-*nitro*-3 : 4-*dimethoxyphenylarsinic acid* did not give an insoluble reduction product, probably on account of the formation of a sulphamic acid (compare this vol., p. 372). It was therefore first reduced to the corresponding *amino*-acid. Further reduction also proceeded abnormally, sodium hyposulphite yielding a yellow, insoluble product containing arsenic in the proportion of three atoms to two benzene nuclei, and hypophosphorous acid a black, insoluble powder containing 93 per cent. of arsenic and probably consisting mainly of the free metalloid.

Bertheim has shown (*Chem. Zeit.*, 1914, **38**, 756; compare D.R.-P. 251104, 254226) that the reduction of molecular proportions of two arsinic acids leads solely to the unsymmetrical arseno-benzene.* More recently, Karrer (*Ber.*, 1916, **49**, 1648) has questioned the accepted mechanism of the reaction, and suggested that the symmetrical arsenobenzenes are first formed and then undergo "double decomposition." The latter suggestion amplifies rather than corrects the former, and indicates why, in spite of three possible, and indeed probable, primary reactions, the product consists solely of the unsymmetrical substance.

The generalisation was later extended (D.R.-P. 270354) to mixtures of an aromatic arsinic acid and an inorganic compound of arsenic, such as sodium arsenite, the products resembling those already referred to. The absence of full analytical data—included in the cases under discussion—has, however, left their composition in doubt, although Morgan ("Organic Compounds of Arsenic and

* At the author's request, Mr. W. H. Gray has confirmed Bertheim's statement by reducing molecular proportions of 1 : 3-benzodiazole-5-arsinic acid (T., 1919, **115**, 1372) and 3-amino-4-hydroxyphenylarsinic acid, the properties and composition of the product confirming the unsymmetric formulation.

Antimony," p. 270) has suggested that they are possibly compounds of tervalent arsenic corresponding with the general types

$$\begin{matrix} R{\cdot}As{:}As \\ | \\ R{\cdot}As{:}As \end{matrix} \quad \text{and} \quad R{\cdot}As{\Big<}\begin{matrix} As \\ | \\ As \end{matrix} \ .$$
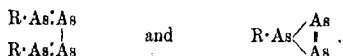
Of the polyarsenides described in the present communication, one—that obtained by the reduction of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid—supports the general formula R_2As_4, whilst another—that from 5-amino-3:4-dimethoxyphenylarsinic acid—agrees with a second type, R_2As_3 or R_4As_6. Of those prepared by Farbwerke vorm. Meister, Lucius & Brüning, one falls into each category.

The assumption of simultaneous reduction would require fission of the arsinic acid to precede reduction. The visual evidence suggests that, in the present instance, the reverse is the case, so the alternative mechanism has been assumed. It is supported by the observation that if a suspension of 3:3'-diamino-4:4'-dihydroxyarsenobenzene in the hyposulphite reduction mixture is treated with two molecular proportions of sodium arsenite and a further quantity of hyposulphite, the transition of the colour through reddish-brown finally to dull brown gradually takes place.

The reaction between two symmetrical arsenobenzenes to produce the unsymmetrical product may be represented as follows:

$$\begin{matrix} R{\cdot}As{\cdot} \\ | \\ R{\cdot}As{\cdot} \end{matrix} + \begin{matrix} {\cdot}As{\cdot}R' \\ | \\ {\cdot}As{\cdot}R' \end{matrix} \rightarrow \begin{matrix} R{\cdot}As{\cdot}As{\cdot}R' \\ | \quad | \\ R{\cdot}As{\cdot}As{\cdot}R' \end{matrix} \rightarrow \begin{matrix} R{\cdot}As{:}As{\cdot}R' \\ \\ R{\cdot}As{:}As{\cdot}R' \end{matrix}$$
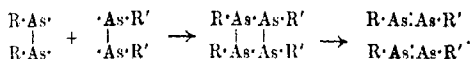
Its extension to the polyarsenical compounds permits of the formulation of the types R_2As_4 and R_4As_6 by the following stages:

$$\begin{matrix} R{\cdot}As{\cdot} \\ | \\ R{\cdot}As{\cdot} \end{matrix} + \begin{matrix} {\cdot}As \\ | \\ {\cdot}As \end{matrix} \rightarrow \begin{matrix} R{\cdot}As{\cdot}As \\ | \quad | \\ R{\cdot}As{\cdot}As \end{matrix} \rightarrow \begin{matrix} R{\cdot}As{\cdot}As{\cdot} \\ | \quad | \\ R{\cdot}As{\cdot}As{\cdot} \end{matrix} + \begin{matrix} {\cdot}As{\cdot}R \\ | \\ {\cdot}As{\cdot}R \end{matrix} \rightarrow$$

$$\begin{matrix} | \\ \downarrow \\ R{\cdot}As{:}As \\ | \\ R{\cdot}As{:}As \end{matrix} \quad \begin{matrix} R{\cdot}As{\cdot}As{\cdot}As{\cdot}R \\ | \quad | \quad | \quad | \\ R{\cdot}As{\cdot}As{\cdot}As{\cdot}R \end{matrix} \text{ or } \begin{matrix} R{\cdot}As{:}As{\cdot}As{\cdot}R \\ | \\ R{\cdot}As{:}As{\cdot}As{\cdot}R \end{matrix}$$

alternatively,

$$\begin{matrix} R{\cdot}As{\cdot} \\ | \\ R{\cdot}As{\cdot} \end{matrix} {>}As{\cdot}As{<} \begin{matrix} {\cdot}As{\cdot}R \\ | \\ {\cdot}As{\cdot}R \end{matrix} \rightarrow \begin{matrix} R{\cdot}As{\diagdown} \\ | \quad As{\cdot}As \\ R{\cdot}As \end{matrix} \begin{matrix} As{\cdot}R \\ | \\ {\diagdown}As{\cdot}R \end{matrix} \ .$$
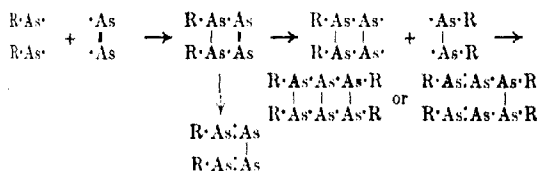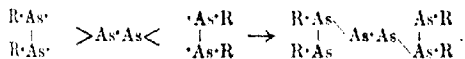
The examination of the polyarsenides has, however, so far been cursory to allow of any final statement as to their constitution.

and it should be emphasised that the homogeneity of the products, assumed on purely chemical grounds, would be difficult to determine satisfactorily in compounds relatively so unstable and insoluble.

EXPERIMENTAL.

p-*Methoxyphenylarsinic Acid.*

This was prepared by the methylation of *p*-hydroxyphenylarsinic acid (*Ber.*, 1914, **47**, 276). The melting point has been variously given by Michaelis (*Ber.*, 1887, **20**, 2051; *Annalen*, 1902, **320**, 299) as 159—160° and 203°, and by Bertheim as 179—180°. The acid crystallised from water in long, prismatic needles, which melted at 182° (corr.), and formed the anhydride at a temperature of 130°, the loss indicating the presence of a quarter of a molecule of water of crystallisation, only removed at the temperature of anhydride-formation   (Found :   loss   at   130° = 9·6,   9·5, $C_7H_9O_4As,\tfrac{1}{4}H_2O$, for loss of $1\tfrac{1}{4}H_2O$, requires 9·5 per cent.   In product : C = 39·4 ; H = 3·4. $C_7H_7O_3As$ requires C = 39·3 ; H = 3·3 per cent.).

As it was thought that this might account for the differences in melting point recorded above, the acid was boiled for an hour with acetic acid containing a little acetic anhydride, and then set aside, when fan-shaped clusters of needles separated. The melting point, however, remained unaltered, although conversion into the anhydride showed the product to be anhydrous (Loss at 130° = 8·1 $C_7H_9O_4As$ requires for loss of $1H_2O$ 7·8 per cent.).

3-*Nitro*-4-*methoxyphenylarsinic Acid.*

To 4·6 grams of *p*-methoxyphenylarsinic acid dissolved in 15 c.c. of sulphuric acid and cooled to −10°, a mixture of 1·4 c.c. of nitric acid (D 1·4) and 1·4 c.c. of sulphuric acid was added, the temperature being kept at about −8°. The mixture, after remaining for twenty-four hours in a cool place, was poured on 100 grams of powdered ice, when an almost colourless, flocculent precipitate deposited, the yield amounting to 95 per cent. of the theoretical.

3-*Nitro*-4-*methoxyphenylarsinic acid* is sparingly soluble in cold water, but readily so in hot, from which it separates in minute needles, which begin to decompose above 290° (Found : C = 30·0 ; H = 3·1 ; N = 5·0 ; OMe = 10·9. $C_7H_8O_6NAs$ requires C = 30·3 ; H = 2·9 ; N = 5·05 ; OMe = 11·2 per cent.). The acid was identical with that obtained by the methylation of 3-nitro-4-hydroxyphenyl-arsinic acid. The product from this reaction, however, contained much unchanged starting material. Separation was effected by

fractional crystallisation, the methylated acid being slightly the less soluble in water.

The *monosodium* salt crystallises in pale yellow needles containing $2H_2O$ (found: loss at $110° = 10·4$. $C_7H_7O_6NAsNa,2H_2O$ requires $H_2O = 10·7$. In dried substance: $Na = 8·0$. $C_7H_7O_6NAsNa$ requires $Na = 7·7$ per cent.).

3-*Amino-4-methoxyphenylarsinic Acid.*

Five grams of 3-nitro-4-methoxyphenylarsinic acid were reduced in boiling methyl alcohol by 120 grams of 5 per cent. sodium amalgam. The solvent was removed by distillation, the residue dissolved in water, the solution decanted from mercury, and neutralised with hydrochloric acid. After concentration, the amino-acid gradually separated, and was purified by crystallisation from water, forming clusters of colourless needles, which melted and decomposed at 193° (corr.) (Found: $N = 5·6$; $OMe = 12·7$. $C_7H_{10}O_4NAs$ requires $N = 5·7$; $OMe = 12·6$ per cent.).

Many attempts were made to displace the amino-group by hydroxyl without success. When the diazotised solution was heated, no evolution of nitrogen took place, whilst experiments in which the temperature of the reaction was raised by the use of 10 per cent. sulphuric acid, a mixture of sodium sulphate and sulphuric acid, or a saturated solution of copper sulphate, led to almost complete decomposition. Similar results were obtained with 3-amino-4-hydroxyphenylarsinic acid. Experiments in which the acids were treated with sodium hydrogen sulphite were equally unsuccessful, and led to fission of the arsinic acid, the only isolable product being a small proportion of the unchanged acid.

4-*Aminoveratrole.*

The reduction of 4-nitroveratrole by tin and hydrochloric acid has already been described (*Bull. Soc. chim.*, 1896, [iii], **15**, 646; T., 1918, **113**, 28). The following method is, however, more satisfactory.

To a solution of 125 grams of crystalline sodium sulphide in a little water, 50 grams of 4-nitroveratrole (T., 1915, **107**, 57) were added, and the mixture was gently boiled for four hours, then cooled, and extracted with chloroform. The crude aminoveratrole was removed from the chloroform by dilute hydrochloric acid, and the combined extracts were basified, when most of the amine separated in a solid state and was collected, any base remaining in the filtrate being extracted by ether. The total yield amounted to 42 grams.

The acetyl derivative is very sparingly soluble in ether or light petroleum, more so in benzene, acetone, or ethyl acetate, and readily so in alcohol or hot water, from which it separates in glistening plates, which melt at 136° (corr.) (compare *Ber.*, 1896, **29**, 2690).

3 : 4-*Dimethoxyphenylarsinic Acid.*

A solution of 15 grams of aminoveratrole in 200 c.c. of 5 per cent. hydrochloric acid was diazotised with 7·1 grams of sodium nitrite, and added to 18 grams of arsenious oxide dissolved in 140 c.c. of 10 per cent. sodium hydroxide, nitrogen being immediately evolved. After several hours, the mixture was rendered strongly alkaline and warmed on the water-bath for half an hour, treated with charcoal, and acidified, when 'the acid gradually separated.

3 : 4-*Dimethoxyphenylarsinic acid* is very sparingly soluble in acetone, but readily so in alcohol or hot water, from which it separates in colourless, anhydrous, rhombic prisms. When placed in a bath at 170°, it melts at 192° (corr.), sintering from 187°. On slow heating, it sinters, but does not melt, between 180° and 190°. This behaviour is due to the readiness with which anhydride-formation takes place (Found : C = 36·4 ; H = 4·2 ; As = 28·6. $C_8H_{11}O_5As$ requires C = 36·6 ; H = 4·2 ; As = 28·6. Loss at 140° = 7·1. $C_8H_{11}O_5As$ requires for loss of $1H_2O$, 6·9 per cent.). The ammoniacal solution yields a voluminous precipitate of minute needles on boiling with calcium chloride, and an amorphous precipitate with magnesia mixture. With warm dilute hypophosphorous acid, a white, amorphous precipitate of 3 : 4 : 3′ : 4′-*tetramethoxyarsenobenzene* is obtained. When heated with hydrobromic acid at 100°, or with hydrochloric acid of varying concentrations at temperatures of 130° to 160° to effect partial demethylation, fission of the arsinic acid grouping takes place, only a small proportion of partly methylated acid being obtained.

5-*Nitro-3 : 4-dimethoxyphenylarsinic Acid.*

The preparation of this acid was carried out as described in the case of 3-nitro-4-methoxyphenylarsinic acid (p. 868), the yield amounting to 85 per cent. of the theoretical. It separates from boiling water in clusters of minute needles, which melt and decompose at 236° (corr.). Reduction with sodium hyposulphite leads to a reddish-brown solution, but no precipitate (Found : C = 31·1 ; H = 3·3 ; N = 4·6 ; As = 24·2. $C_8H_{10}O_7NAs$ requires C = 31·3 ; H = 3·3 ; N = 4·6 : As = 24·4 per cent.).

The *monosodium* salt crystallises in glistening, flattened prisms, which lose their lustre when dried in the air and contain $6H_2O$ (Found: loss at $110° = 24·7$. $C_8H_9O_7NAsNa,6H_2O$ requires $H_2O = 24·7$. In dried material, $Na = 6·9$. $C_8H_9O_7NAsNa$ requires $Na = 7·0$ per cent.).

The *barium hydrogen* salt crystallises as a matted mass of faintly yellow needles, which contain $3H_2O$ (Found: loss at $110° = 6·7$. $(C_8H_9O_7NAs)_2Ba,3H_2O$ requires $H_2O = 6·7$. In dried material, $Ba = 18·2$. $(C_8H_9O_7NAs)_2Ba$ requires $Ba = 18·3$ per cent.).

Although the acid is more stable towards mineral acids than 3:4-dimethoxyphenylarsinic acid, its hydrolysis does not afford a suitable means of preparing the corresponding partly methylated and demethylated acids. At 160° with concentrated hydrochloric acid, it is largely decomposed, but at 130° slow hydrolysis of the methoxyl groups takes place, and crystallisation of the product yields from the more soluble fractions a proportion of a partly methylated acid, separating from water in slender prisms and melting and decomposing at about 254° (corr.). It is apparently identical with *5-nitro-3-hydroxy-4-methoxyphenylarsinic acid* (p. 874) (Found: $C = 28·9$; $H = 3·0$; $OMe = 11·0$. $C_7H_8O_7NAs$ requires $C = 28·7$; $H = 2·75$; $OMe = 10·6$ per cent.).

5-Amino-3:4-dimethoxyphenylarsinic Acid.

The foregoing acid was reduced by ferrous hydroxide in alkaline solution (compare *J. Amer. Chem. Soc.*, 1918, **40**, 1581), the yield amounting to about 85 per cent. of the theoretical. *5-Amino-3:4-dimethoxyphenylarsinic acid* dissolves sparingly in cold water or alcohol, but readily in dilute mineral acids or hot water, from which it separates in radiating clusters of needles melting and decomposing at 173° (corr.). The solution in dilute hydrochloric acid gives a bright red coloration with a trace of potassium dichromate, and, after treatment with nitrous acid, a deep red coloration with sodium-β-naphthoxide. The aqueous solution develops a reddish-brown colour with ferric chloride. The ammoniacal solution gives no precipitate on warming with magnesia mixture or with barium chloride, but with calcium chloride a heavy, crystalline precipitate (Found: $N = 5·0$; $As = 27·3$. $C_8H_{12}O_5NAs$ requires $N = 5·05$; $As = 27·05$ per cent.).

Reduction of 5-Amino-3:4-dimethoxyphenylarsinic Acid.

(*a*) *With Sodium Hyposulphite.*—The reduction was carried out as described in the case of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid (p. 873). The pale yellow precipitate deepened in colour as

the reaction proceeded. It was collected, washed very thoroughly with water and with alcohol, and dried in a vacuum, first at the ordinary temperature, and finally at 60° for analysis. The ratio of arsenic to the other elements present indicated 3 atoms of arsenic to 2 benzene nuclei. It dissolves sparingly in the usual organic solvents, but readily in dilute acids (Found : $C = 37.3$, 37.3; $H = 4.0$, 3.9; $N = 5.2$; $As = 41.4$. $C_{16}H_{20}O_4N_2As_3$ requires $C = 36.3$; $H = 3.8$; $N = 5.3$; $As = 42.5$ per cent.).

(*b*) *With Hypophosphorous Acid.*—Reduction with dilute hypophosphorous acid at 60° yielded a black precipitate, which was isolated as in the previous instance (Found : $As = 93.0$; $C = 2.6$, 2.9; $H = 0.54$, 0.60).

The composition of these products is discussed in the introduction.

4-Hydroxy-3-methoxyphenylarsinic Acid.

A suspension of 25.2 grams of 4-nitroguaiacol in 90 c.c. of concentrated hydrochloric acid was reduced by the gradual addition of 42 grams of tin. The resulting solution was freed from tin, diazotised with 12 grams of sodium nitrite, and added to an ice-cold solution of 27 grams of arsenious acid in 210 c.c. of 10 per cent. sodium hydroxide, the solution being maintained distinctly alkaline. As soon as the evolution of nitrogen ceased, the product was heated for half an hour on the water-bath, acidified to methyl-orange by means of hydrochloric acid, treated with charcoal to remove coloured impurities, evaporated to dryness under diminished pressure, and extracted with alcohol. The extract, amounting to about 25 grams, was dissolved in boiling water, when, after separation of a small quantity of a very sparingly soluble substance (*A*), 12.5 grams of *4-hydroxy-3-methoxyphenylarsinic acid* were obtained. The acid is sparingly soluble in cold water or alcohol, but readily so in acetic acid or in hot water, from which it separates in stout, glistening, rhombic prisms containing $1H_2O$. After drying at 110°, it melts at 190° (corr.) (Found : loss at $110° = 7.1$. $C_7H_9O_5As, H_2O$ requires 6.8. In dried material, $C = 34.2$; $H = 3.8$; $As = 30.3$. $C_7H_9O_5As$ requires $C = 33.9$; $H = 3.7$; $As = 30.2$ per cent.). The ammoniacal solution gives no precipitate on boiling with barium chloride or magnesia mixture, but yields a crystalline precipitate of the *calcium* salt with calcium chloride. On warming the acid with a dilute solution of hypophosphorous acid, a colourless precipitate of *4 : 4′-dihydroxy-3 : 3′-dimethoxyarsenobenzene* is obtained.

The *acetyl* derivative crystallises from ethyl acetate containing a little alcohol in colourless, glistening plates, which melt at 186° (corr.), sintering from 182°. It is readily soluble in water or

alcohol, but sparingly so in ether or ethyl acetate (Found: $\mathrm{C}=37\cdot5$; $\mathrm{H}=4\cdot1$. $\mathrm{C_9H_{11}O_6As}$ requires $\mathrm{C}=37\cdot25$; $\mathrm{H}=3\cdot8$ per cent.).

The sparingly soluble material (A), which was isolated only in minute quantity, proved to be 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxy-diphenylarsinic acid*. It separated from much water in radiating clusters of minute prisms containing $1\tfrac{1}{2}\mathrm{H_2O}$, and melted at 234° (corr.), sintering from 227°. The ammoniacal solution of the acid gave a precipitate on warming with barium chloride, but not with magnesia mixture (Found: loss at 110° = 6·7. $\mathrm{C_{14}H_{15}O_6As,1\tfrac{1}{2}H_2O}$ requires 7·0. In dried material, $\mathrm{C}=47\cdot3$; $\mathrm{H}=4\cdot4$; $\mathrm{As}=21\cdot2$. $\mathrm{C_{14}H_{15}O_6As}$ requires $\mathrm{C}=47\cdot5$; $\mathrm{H}=4\cdot3$; $\mathrm{As}=21\cdot2$ per cent.).

5-*Nitro*-4-*hydroxy*-3-*methoxyphenylarsinic Acid*.

The nitration of 4-hydroxy-3-methoxyphenylarsinic acid was carried out as already described (compare p. 868). Separation did not take place until the bulk of the mineral acid was neutralised by the addition of anhydrous sodium carbonate, when 3·2 grams of the nitro-acid were obtained. On crystallisation from boiling water, it formed glistening leaflets, which decomposed gradually above 260° without melting (Found: $\mathrm{As} = 25\cdot5$; $\mathrm{N} = 4\cdot8$. $\mathrm{C_7H_8O_7NAs}$ requires $\mathrm{As} = 25\cdot6$; $\mathrm{N} = 4\cdot8$ per cent.).

On warming with a dilute solution of hypophosphorous acid, a bright yellow, granular precipitate of 5 : 5′ *dinitro*-4 : 4′-*dihydroxy*-3′-*dimethoxyarsenobenzene* was obtained.

5 : 5′-*Diamino*-4 : 4′-*dihydroxy* 3 : 3′-*dimethoxyarsenobenzene*.

To a solution of 3·5 grams of the above acid in 60 c.c. of water and 12 c.c. of 2N-sodium hydroxide was added a solution of 3 grams of sodium hyposulphite and 10 grams of magnesium chloride in 170 c.c. of water. The mixture was heated in an atmosphere of carbon dioxide at 60° for one and a-half hours, the arsenobenzene then collected, washed with water, dissolved in methyl alcohol containing hydrogen chloride, and the hydrochloride precipitated by the addition of dry ether. The product amounted to 2·1 grams of a faintly yellow powder, readily soluble in water and methyl alcohol, less so in ethyl alcohol, and insoluble in ether or acetone. The aqueous solution reacts faintly acid to methyl-orange. When dried to constant weight in a vacuum over sulphuric acid, it retains solvent equivalent to two molecules of water. It decomposes sharply at 186° (corr.). The addition of dilute sulphuric acid to the aqueous solution does not cause precipitation of the sulphate, but concentrated hydrochloric acid causes precipitation of the *hydrochloride* (Found: As 27·9; $\mathrm{N} = 5\cdot1$;

$Cl = 12.7$. $C_{14}H_{16}O_4N_2As_2,2HCl,2H_2O$ requires $As = 28.0$; $N = 5.2$; $Cl = 13.2$ per cent.). This substance was submitted to biological test by Dr. R. A. O'Brien, of the Wellcome Physiological Research Laboratories, the results indicating that it was only slightly more toxic than salvarsan.

3-Hydroxy-4-methoxyphenylarsinic Acid.

This acid was prepared from 5-nitroguaiacol in the same manner as 4-hydroxy-3-methoxyphenylarsinic acid (p. 872) was obtained from 4-nitroguaiacol. From 21 grams of the nitroguaiacol, 8 grams of the pure acid were obtained. 3-*Hydroxy-4-methoxyphenyl-arsinic acid* separates from water in short, stout, flattened prisms containing one molecule of the solvent, which is lost at 110°. It then melts at 189° (corr.). The pure acid dissolves sparingly in alcohol or the other usual organic solvents (Found: loss at $110° = 7.3$. $C_7H_9O_5As,H_2O$ requires 6.8.   In dried material, $C = 34.2$; $H = 3.8$; $As = 30.1$. $C_7H_9O_5As$ requires $C = 33.9$; $H = 3.7$; $As = 30.2$ per cent.). The ammoniacal solution gives no precipitate on boiling with barium chloride or magnesia mixture, but yields a precipitate with calcium chloride. On warming with a dilute solution of hypophosphorous acid, the acid yields a colour-less precipitate of 3 : 3'-*dihydroxy*-4 : 4'-*dimethoxyarsenobenzene*.

The *acetyl* derivative crystallises from benzene containing a little alcohol in woolly needles, which decompose gradually above 200°. It is readily soluble in water, alcohol, or ethyl acetate, but very sparingly so in benzene or light petroleum (Found: $C = 37.5$; $H = 4.0$. $C_9H_{11}O_6As$ requires $C = 37.25$; $H = 3.8$ per cent.)

5-Nitro-3-hydroxy-4-methoxyphenylarsinic Acid.

The preparation of this acid was carried out in a similar manner to that of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid (p. 873); the yield amounted to 80 per cent. of the theoretical. The acid crystallises from water, in which it is somewhat sparingly soluble, in stellate clusters of prismatic needles, which melt at 252° (corr.), darkening gradually above 220° (Found: $As = 25.6$; $N = 5.0$. $C_7H_8O_7NAs$ requires $As = 25.6$; $N = 4.8$ per cent.). On reduction with warm hypophosphorous acid, it yields a bright yellow pre-cipitate of 5 : 5'-*dinitro*-3 : 3'-*dihydroxy*-4 : 4'-*dimethoxyarseno-benzene*.

Reduction of 5-Nitro-3-hydroxy-4-methoxyphenylarsinic Acid.

The reduction was carried out, using sodium hyposulphite, as already described. The pale yellow precipitate first formed

gradually darkened to brick-red as the reaction proceeded. It was collected, washed thoroughly with water, and dissolved in methyl alcohol containing hydrogen chloride, forming a blood-red solution, which deposited a reddish-brown precipitate of the *hydrochloride* in addition of ether. Analysis indicated that the product contained 2 atoms of arsenic to each benzene nucleus (Found: C = 25·9; H = 3·3; N = 4·1; Cl = 10·5; As = 45·6. $C_{14}H_{16}O_4N_2As_4,2HCl$ requires C = 25·9; H = 2·8; N = 4·3; Cl = 10·9; As = 46·2 per cent.).

3'-*Amino*-4'-*hydroxy*-1 : 3-*diazole*-5 : 1'-*arsenobenzene*,
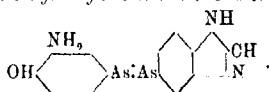
A mixture of molecular proportions of 3-amino-4-hydroxyphenyl-arsinic acid and 1 : 3-benzodiazole-5-arsinic acid was reduced with sodium hyposulphite in the manner previously described. The product was converted into the hydrochloride by solution in methyl alcohol containing hydrogen chloride, and precipitation by ether. The yield amounted to about 85 per cent. of the theoretical.

The *hydrochloride* forms a pale yellow powder, readily soluble in water or methyl alcohol, less so in ethyl alcohol, and almost insoluble in ether or acetone. After drying for several hours in a vacuum over sulphuric acid, it retains solvent approximating to 3 molecules of water of crystallisation, of which one is lost at 60° and a second at 100° in a vacuum. On heating, it decomposes at 240° (corr.) (Found: C = 32·1; H = 3·8; N = 8·3; As = 30·4; Cl = 14·0. $C_{14}H_{11}ON_3As_2,2HCl,3H_2O$ requires C = 31·1; H = 3·8; N = 8·4; As = 29·9; Cl = 14·1 per cent. Loss at 60° in a vacuum = 7. Loss of $1H_2O$ requires 3·6. Loss at 100° in a vacuum = 7·3. Loss of $2H_2O$ requires 7·2 per cent.).

The *base* dissolves readily and completely in sodium hydroxide or in methyl alcohol containing hydrogen chloride, thus differing distinctly from 5 : 5'-arseno-1 : 3 : 1' : 3'-benzodiazole (T., 1919, **115**, 372), which dissolves but sparingly in the former and is quite insoluble in the latter.

In conclusion, the author would thank Mr. F. P. Walton for assistance in the analysis of a number of the compounds described in the investigation.

XCVIII.—2 : 3 : 6-*Trinitrotoluene : a New Synthesis*.

By OSCAR LISLE BRADY and ARTHUR TAYLOR.

2:3:6-TRINITROTOLUENE was the last of the six isomeric trinitro-
toluenes to be obtained. Molinari and Giua (*Zeitsch. ges Schiess.
u. Sprengstoffw.*, 1914, **9**, 239), from the oily residues obtained in
the purification of commercial trinitrotoluene, isolated a compound
(m. p. 79·5°), unaltered by further crystallisation from alcohol,
which gave analytical figures corresponding with trinitrotoluene.

As this differed from the five known isomerides, it was considered
by them to be the 2:3:6-compound. Körner and Contardi, how-
ever (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339), synthesised this
compound from 2:4:6-trinitrotoluene by the following series of
transformations: 2:4:6-trinitrotoluene ⟶ 2:6-dinitro-*p*-toluidine
⟶ 3-bromo-2 : 6-dinitro-*p*-toluidine ⟶ 3-bromo-2 : 6-dinitro-
toluene ⟶ 2:6-dinitro-*m*-toluidine ⟶ 2:3:6-trinitrotoluene.

The 2:3:6-trinitrotoluene obtained in this way melted at 111°.
Molinari and Giua's compound probably consisted of a mixture of
2:3:4- and 3:4:6-trinitrotoluenes, as in the separation of the mix-
ture of these compounds, obtained by the nitration of *m*-nitro-
toluene, by crystallisation from alcohol, a substance is obtained of
approximately the melting point given by Molinari and Giua
which crystallises from alcohol unchanged, but can be further
fractionated into its two components by alternate crystallisation
from acetic acid and from alcohol. This substance, of constant
melting point, seems to be a loose, molecular compound of the two
isomerides, as there is evidence of the existence of a compound of
this melting point from the binary fusion diagram of 2:3:4- and
3:4:6-trinitrotoluenes (private communication from Dr. W. H.
Gibson).

Körner and Contardi state that they have found conditions of
reduction under which 2:4:6-trinitrotoluene gives a 60 per cent
yield of 2:6-dinitro-*p*-toluidine and promise a description in a
subsequent paper. This has not yet been published and, as the
usual means of reduction give poor yields, an alternative method
has been devised for the preparation of 2:3:6-trinitrotoluene from
2:6-dinitrotoluene.

The reactions involved are summarised on p. 877.

The yields are satisfactory at all stages of the process, and a
considerable quantity of 2:3:6-trinitrotoluene has been prepared
by this method.

$$
\begin{array}{ccc}
\text{Me} & \text{Me} & \text{Me} \\
\text{NO}_2\!\!\bigcirc\!\!\text{NO}_2 \rightarrow & \text{NO}_2\!\!\bigcirc\!\!\text{NH}_2 \rightarrow & \text{NO}_2\!\!\bigcirc\!\!\text{NHAc}
\end{array}
$$

Me

NO$_2$|180°| NHAc
NO$_2$

Me

NO$_2$|209| NHAc
NO$_2$

Me

[O$_2$|216| NH$_2$ →
[O$_2$

Me

NO$_2$
NO$_2$

Me

NO$_2$
NO$_2$ ←

Me

NO$_2$|151| NH$_2$
NO$_2$

Me

[O$_2$ NO →
[O$_2$

Me

NO$_2$ NO$_2$
NO$_2$ ←

Me

NO$_2$ NO
NO$_2$
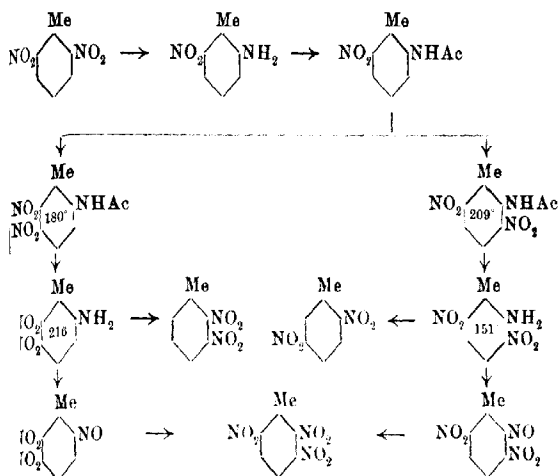
The mixture of the two dinitrotoluidines obtained by the nitra-
on of 6-nitroaceto-o-toluidide and subsequent hydrolysis has been
parated, and the dinitrotoluidines have been oriented by elimina-
on of the amino-group and conversion into 2:3- and 2:5-dinitro-
luenes. This separation is not necessary for the synthesis of the
:3:6-trinitrotoluene, as both compounds are converted into it in
he subsequent operations.

EXPERIMENTAL.

Reduction of 2:6-Dinitrotoluene.—Although the preparation of
itro-o-toluidine by the reduction of 2:6-dinitrotoluene has been
ntioned by Cunerth (*Annalen*, 1874, **172**, 223), Bernthsen (*Ber.*,
2, **15**, 3017), Noelting (*Ber.*, 1904, **37**, 1018), and Tatschaloff
pr. Chem., 1902, [ii], **65**, 239), no experimental details are
en. The following method has been found to give good yields.
50 grams of 2:6-dinitrotoluene in 100 c.c. of boiling alcohol are
led gradually 280 c.c. of ammonium sulphide (15 per cent.), the
xture being shaken thoroughly between each addition. When
the ammonium sulphide has been added, the mixture is heated
the water-bath for fifteen minutes and then cooled. The pre-
itate is collected, washed with water, extracted with hot dilute
drochloric acid, and the solution filtered. The residue, consist-
g of the sparingly soluble hydrochloride of the base and sulphur,
repeatedly extracted with hot water containing a small quantity

of hydrochloric acid until the filtrate no longer gives a precipitat, on adding ammonia. The hydrochloric acid and aqueous extract are rendered alkaline with ammonia, cooled, and the 6-nitro-o toluidine collected and dried at 70°. The yield is 80 per cent. of the theoretical.

Acetylation of 6-Nitro-o-toluidine.—Twenty-five grams of 6-nitro o-toluidine are added to 35 c.c. of acetic anhydride, followed by one drop of concentrated sulphuric acid. Vigorous action takes place, and the acetyl compound separates at once. A further quantity can be obtained from the filtrate by pouring into water. It separates from alcohol in colourless needles melting at 163—164° (Lellman and Würthner, *Annalen*, 1885, **228**, 241, give 158°). The yield of recrystallised product is 80 per cent. of the theoretical.

Nitration of 6-Nitroaceto-o-toluidide and Hydrolysis of the Product.—To 175 c.c. of mixed acid (in the proportion of 5 c.c. of nitric acid, D 1·5, to 8 c.c. of concentrated sulphuric acid) cooled in ice, 25 grams of 6-nitroaceto-o-toluidide are added in small portions at a time, the temperature being kept between 4° and 7° The solid dissolves slowly, and when all has been added, th temperature is allowed to rise to 12°. By this time, all the nitro acetotoluidide will have dissolved, and the product is slowly pourec into a litre of water with thorough stirring. A pure, white product is precipitated in theoretical yield. This is collected, washed dried, and 31 grams are dissolved in 100 c.c. of concentrated sulphuric acid and warmed on the water-bath for two hours. The mixture is cooled and poured into cold water, when a mixture of 5:6- and 3:6-dinitro-o-toluidines is precipitated in theoretical yield as a bright orange-yellow, crystalline material melting at 138—200°.

Separation of the Dinitro-o-toluidines.—By fractional crystallisation of the mixed dinitrotoluidines, a compound (m. p. 216°) is obtained, which was proved to be 5:6-dinitro-o-toluidine (see below). It is not possible to obtain the other isomeride pure by this method, and repeated crystallisation of the mixed acetyl derivatives gives a compound melting at 180°, which, however, on hydrolysis yields 5:6-dinitro-o-toluidine.

The more readily soluble amino-compound may be obtained, however, by dissolving the mixture of amines in hot glacial acetic acid and cooling slowly. Two kinds of crystals separate, namely, fine yellow needles and large orange prisms and, after filtering and washing with light petroleum, these can be readily separated by sieving. The orange crystals, when recrystallised from alcohol, yielded 3:6-dinitro-o-toluidine (m. p. 151°), previously obtained by Körner and Contardi (*loc. cit.*) by the action of ammonia on 2:3:6-trinitrotoluene, but not fully described.

5:6-*Dinitro-o-toluidine* crystallises from alcohol in fine, deep
yellow needles melting at 216° (Found: N = 21·3. $C_7H_7O_4N_3$
requires N = 21·3 per cent.).

5:6-*Dinitroaceto-o-toluidide* crystallises from acetic acid in large
white crystals melting at 180° (Found: N = 17·4. $C_9H_9O_5N_3$
requires N = 17·6 per cent.).

3:6-Dinitro-*o*-toluidine crystallises from alcohol in brilliant
range prisms melting at 151° (Found: N = 21·5.   Calc.: N = 21·3
er cent.).

3:6-*Dinitroaceto-o-toluidide*, obtained from the above by treat-
ment with acetic anhydride in the presence of a trace of concen-
trated sulphuric acid, crystallises from alcohol in very pale yellow,
microscopic prisms melting at 209° (Found: N = 17·5. $C_9H_9O_5N_3$
requires N = 17·6 per cent.).

Orientation of the Dinitro-o-toluidines.—The position of the
second nitro-group in these compounds has been determined by
conversion into the dinitrotoluenes by elimination of the amino-
group.

Of the compound melting at 216°, 2 grams were dissolved in a
mixture of 10 c.c. of fuming sulphuric acid (containing 20 per cent.
of sulphur trioxide) and 40 c.c. of absolute alcohol (freshly distilled
over calcium oxide), and the mixture was heated on the steam-
ath. Six grams of finely powdered, dried sodium nitrite were
added in small portions with vigorous shaking. Most of the
alcohol was then distilled off, water added, and the mixture dis-
tilled in a current of steam. The dinitrotoluene which distilled
was collected, and, after recrystallisation from dilute alcohol, proved
o be 2:3-dinitrotoluene from its melting point and mixed melting
point with another sample. The compound melting at 216° is
therefore 5 : 6-dinitro-*o*-toluidine.

In a similar way, 2:5-dinitrotoluene was obtained from the com-
pound melting at 151°, which is accordingly 3 : 6-dinitro-o-toluidine.

Preparation of 2 : 3 : 6-*Trinitrotoluene.*—For the preparation of
the trinitrotoluene, it is not necessary to separate the dinitro-o-
toluidines, as both these compounds, on displacement of the amino-
by the nitro-group, yield the same derivative.

Two methods of conversion were investigated, namely, introduc-
tion of the nitro-group through the diazonium nitrate (compare
Itt. *Ber.*, 1909, **42**, 2953) and direct oxidation of the amino-
group with Caro's acid, followed by nitric acid.

Of these, the first, under varying conditions, was completely
unsuccessful, but no difficulty was experienced with the second.

To a solution of Caro's acid, prepared from 60 grams of finely
powdered ammonium persulphate and 44 c.c. of concentrated

sulphuric acid, the mixture being finally poured on 120 grams of crushed ice, is added a solution of 12 grams of the dinitrotoluidines in 36 c.c. of concentrated sulphuric acid. A yellow solid separates at once, and the mixture is allowed to remain, with frequent shaking, for some days. At the end of that time the mixture of dinitronitrosotoluenes is collected and dropped in small quantities at a time into 100 c.c. of nitric acid (D 1·5) heated on the water-bath. When nitrous gases are no longer evolved and the liquid assumes a pale colour, it is diluted somewhat and cooled, when the 2:3:6-trinitrotoluene separates in colourless needles. The compound, after being collected and washed with water, is almost pure but may be recrystallised from alcohol.

The yield of 2:3:6-trinitrotoluene prepared in this way is from 50 to 60 per cent. of the 2:6-dinitrotoluene employed.

In conclusion, the authors wish to express their thanks to the Director of Artillery for permission to publish these results.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH.   [Received, June 22nd, 1920.]

XCIX.—The Effect of Reducing Agents on Tetranitro-methane, and a Rapid Method of Estimation.

By AILEEN BAILLIE, ALEXANDER KILLEN MACBETH, and
NORAH IRENE MAXWELL.

PREVIOUS work by one of us (T., 1915, 107, 87) indicated that tetranitromethane contained one labile nitro-group, and it appeared likely that this would be removed in reduction, so that guanidine seemed the most probable product of extreme reduction. Acid reduction experiments with tin and nickel-coated zinc carried out by Rakshit (J. Amer. Chem. Soc., 1914, 36, 1221) resulted in the production of guanidine. A study of alkaline and electrochemical reduction methods has been undertaken by us, and in this paper the effect of some alkaline reducing agents is recorded. It is hoped to communicate later the results of electrochemical methods.

The reductions now described have resulted in the removal of the labile "nitroite" group, with the production of salts of nitroform which may be conveniently and safely prepared by the methods described. The procedure consisted in agitating the nitro

compound with aqueous solutions of the reducing agents containing requisite amount of potassium hydroxide, which neutralises the nitroform produced, precipitating it as the sparingly soluble potassium salt. The solutions are thereby prevented from becoming acid, and secondary action with the reducing agent is avoided. Aqueous potassium hydroxide itself attacks tetranitromethane, with the formation of the potassium salt of nitroform, together with nitrate, nitrite, and carbonate of potassium, the quantities of which vary with concentration. The decomposition in such case, however, is much slower than when a reducing agent is present, and in the latter case the tetranitromethane is generally all converted into nitroform without the loss entailed in the formation of potassium carbonate.

Results have been obtained, amongst others, with sodium sulphite, potassium sulphite, sodium potassium tartrate, and hydrazine. In all cases, the nitroform salt has been identified by estimation of the percentage of potassium contained in the salt recrystallised from water; this was decomposed by sulphuric acid and the potassium weighed as sulphate.

Other reducing agents have also been tried with success; potassium phosphite and potassium sulphide may be mentioned as instances. In the case of the sulphide, much sulphur is precipitated, from which the nitroform salt is removable only with some difficulty. Aqueous solutions of sulphur dioxide do not attack tetranitromethane even after long-continued shaking. Ammonium sulphide readily decomposes it, but in this case the reduction seems to be carried past the nitroform stage, and the products, as yet, have not been identified.

Sodium Sulphite.—On shaking an aqueous solution of sodium sulphite with tetranitromethane, the solution gradually becomes coloured, and the odour of tetranitromethane ultimately disappears. Nitrous fumes are evolved as the reaction proceeds, and the solution becomes acid. If sodium hydroxide is added to the solution at the beginning of the reaction, the decomposition is more satisfactory, and if the solution does not become acid, there is no evolution of nitrous fumes. When the reduction is complete, the solution contains the sodium salt of nitroform, and responds to tests for nitrites and sulphates. Sodium hydroxide is used up in the reaction, and if sufficient is not present the solution becomes acid. The reaction proceeds according to the equation

$$(NO_2)_4C \cdot Na_2SO_3 \cdot 2NaOH = (NO_2)_3CNa \cdot Na_2SO_4 \cdot NaNO_2 \cdot H_2O.$$
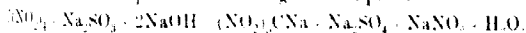
In an actual experiment, 40 grams of sodium sulphite were dissolved in 300 c.c. of water, sodium hydroxide solution being present. Eighteen grams of tetranitromethane were added, and

the mixture was shaken for half an hour. Sodium hydroxide was
added at intervals as required. After about an hour, the odour
of tetranitromethane had completely disappeared, and the solution
was deep orange. No nitroform salt separated out, but, on acidify-
ing with sulphuric acid and extracting with ether, nitroform was
obtained. The yield may be ascertained by adding potassium
alkyloxide to an aliquot part of the ethereal solution to precipitate
the characteristic potassium salt. The yield of potassium salt from
the above quantities was 12 grams.

Potassium Sulphite.—The use of this is preferable to sodium
sulphite, since the sparingly soluble potassium salt of nitroform is
precipitated, and may be isolated by filtration. The solution is
liable to become acid during the process, and small quantities of
potassium hydroxide solution must be added at intervals. After
the experiment, the solution responds to tests for sulphate, and it
is therefore evident that the initial strength of the sulphite solution
must be such that the less soluble sulphate will not finally be
present in quantities sufficient to saturate the solution and
crystallise out, contaminating the nitroform salt.

Arsenious Acid.—This proves a very good reducing agent,
degrading tetranitromethane to the nitroform salt in a short time.
In a typical experiment, 25 grams of arsenious oxide were dis-
solved in 200 c.c. of water, a sufficient quantity of potassium hydr-
oxide being added. On the addition of 10 grams of tetranitro-
methane, the yellow nitroform salt separated out after a little
vigorous shaking. After a short time, the tetranitromethane was
completely decomposed, and 7·8 grams of dry nitroform salt were
collected. The crystals so obtained are dull yellow, but, after re-
crystallisation from water, have the characteristic yellow appear-
ance of the pure salt. The filtrate responds to the usual tests for
nitrites and arseniates.

Hydrazine.—Preliminary experiments indicated that tetranitro-
methane was rapidly acted on by hydrazine, nitrogen being evolved.
In an experiment on a larger scale, 20 grams of hydrazine sulphate
and 40 grams of potassium hydroxide were added to 500 c.c. of
water. Thirty grams of tetranitromethane were then added in
small quantities, the mixture being gently shaken in an unstoppered
bottle. The potassium salt of nitroform rapidly separated, and
the reduction was complete in a quarter of an hour. Twenty-five
grams of the dry nitroform salt were collected from this experi-
ment. The reaction proceeds according to the equation

$$NH_2 \cdot NH_2 + 2C(NO_2)_4 + 4KOH = 2(NO_2)_3CK + 2KNO_2 + N_2 + 4H_2O.$$
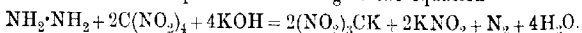
It appeared probable that a method for estimating tetranitro-
methane could be based on this reaction, and it is found that the

method gives results within the limit of experimental error. Half a gram of tetranitromethane is a convenient amount to use, as it liberates some 30 c.c. of nitrogen from hydrazine solutions. As the estimation is carried out in a Lunge nitrometer graduated to 0·2 c.c., the experimental error in reading the volume of gas evolved in the reaction may well be this amount. From the quantitative relation given above, 0·2 c.c. of nitrogen corresponds approximately with 0·0035 gram of tetranitromethane. Using half a gram of the nitro-compound, the error in reading the nitrometer should theoretically be within a margin of 1 per cent. The results obtained are well within this limit.

Phenylhydrazine has been substituted for hydrazine in some observations, but the volume of nitrogen liberated was some three times greater than the calculated quantity. The reduction with this reagent is evidently carried past the nitroform stage, and in actual experiments, phenylhydrazine was found to liberate more than the additional two volumes when it acted on the potassium salt of nitroform.

As hydrazine itself does not attack the nitroform salt, the method can be applied to estimate tetranitromethane in solutions which also contain nitroform, and since the reaction takes place in the presence of excess of potassium hydroxide, it may be used for estimation of solutions containing nitrous and nitric or other mineral acid in addition to the nitro-compound.

In the estimation, a Lunge nitrometer is filled with mercury, as in the Crum method of estimating nitrates. A 10 per cent. solution of tetranitromethane in alcohol is of a convenient strength for use. The nitro-compound was purified by repeated washings with water and by subsequently freezing and melting several times. It was colourless and melted at about 13·4°. The hydrazine solution is prepared by adding 10 grams of hydrazine sulphate and 20 grams of potassium hydroxide to about 80 c.c. of water, filtering, and diluting to 100 c.c. Five c.c. of the freshly prepared hydrazine solution contain an excess of the reagents required by 5 c.c. of the tetranitromethane solution. One c.c. of the hydrazine solution is introduced into the nitrometer, and the last traces are washed in with small quantities of water. This acts as a cushion, which prevents contact of the solution of the nitro-compound with the mercury. Five c.c. of the tetranitromethane solution are now carefully introduced and washed in with alcohol. This solution floats on the top of the hydrazine solution previously introduced, and little reaction takes place. Four more c.c. of the hydrazine solution are now added, and, on falling through the tetranitromethane solution, a reaction rapidly ensues. Nitrogen is quickly

evolved, and the potassium salt of nitroform is precipitated. On account of the rapidity with which the nitrogen is evolved, it is imperative to have the mercury poured out of the side-limb of the nitrometer before the introduction of the hydrazine solution. If this is not done, there is an inevitable loss of nitrogen, as the mercury is driven down quickly, and consequent pressure develops almost immediately.   The main reaction is over in less than a minute, but further traces of nitrogen are evolved on shaking once to mix the solutions thoroughly. As the reaction is exothermic, the nitrometer must be allowed to remain for some time before a volume reading is taken.

Sodium hydroxide may be substituted for potassium hydroxide, but the latter is preferable. The following are typical results, obtained at various times by different observers. Five c.c. of a 10 per cent. solution of tetranitromethane in alcohol were taken in each case, and the weights of tetranitromethane in 100 c.c. of solution were found to be: (1) 9·938; (2) 9·904; (3) 9·994; (4) 9·926 grams.

It is therefore evident that the reduction of tetranitromethane by hydrazine is quantitative, and the reaction affords an easy and rapid method for estimating the nitro-compound. Conversely, standard solutions of tetranitromethane may be employed in the estimation of hydrazine in solutions of its salts.

THE CHEMICAL LABORATORIES,
    QUEEN'S UNIVERSITY,
        BELFAST.

THE Council has ordered the following letter and report to be printed in the Journal of the Society:

<div align="center">
WHINFIELD,
SALCOMBE,
S. DEVON,
July 10th, 1920.
</div>

GENTLEMEN,

I beg to submit the Report of the International Committee on Atomic Weights for 1920–1921, to which I have affixed, by his desire, the signature of Prof. Urbain.

The Report deals with the atomic weights of fluorine, silicon, lead (isotopic), tellurium, scandium, and samarium; and draws attention to the critical work of Guye on the reduction of experimental data, and to the paper of Van Laar on the method of calculating atomic weights.

Certain of the newly published values are confirmatory of those already in use; others are preliminary, and fuller details are promised. The only change at present suggested is in the case of scandium, namely, from 44·1 to 45·1, which appears to be fully justified by the experimental evidence.

<div align="center">
1 am, Gentlemen,
Your obedient Servant,
T. E. THORPE.
</div>

The Hon. Secretaries,
The Chemical Society,
London.

Report of the International Committee on Atomic Weights for 1920-1921.

Since the report of this committee for the preceding year was prepared, only a few new determinations of atomic weights have been published. They may be summarised as follows:

Fluorine.—Moles and Batuecas (*J. Chim. Phys.*, 1919, **17**, 538) have made twenty-three determinations of the density of methyl fluoride, CH_3F. For the weight of a normal litre of the gas, they find, in mean, 1·54542 grams. From this the molecular weight, 34·024, is deduced, and $F = 18·996$. This, rounded off to 19, is the value already accepted.

<div align="right">L L 2</div>

Silicon.—Baxter, Weatherill, and Holmes (*J. Amer. Chem. Soc.*, 1920, **42**, 1194), from analyses of silicon tetrachloride, find $Si = 28 \cdot 111$. This determination, however, is not regarded by the authors as final. Its acceptance, therefore, must await confirmation, especially as the value is much lower than that given in the present table of atomic weights.

Lead.—The atomic weight of isotopic lead from thorium minerals has been determined by Hönigschmid (*Zeitsch. Elektrochem.*, 1919, **25**, 91). For lead from Norwegian thorite, he finds $Pb = 207 \cdot 88$ to $207 \cdot 92$. For lead from Ceylonese thorianite, $Pb = 206 \cdot 88$ to $207 \cdot 24$. In thorianite, there is evidently a mixture of isotopes, and perhaps also of normal lead.

Richards and Sameshima (*J. Amer. Chem. Soc.*, 1920, **42**, 929) have examined lead from a radioactive Japanese mineral. The values found for the atomic weight were $207 \cdot 11$, $207 \cdot 12$, and $207 \cdot 15$. For ordinary lead, the corresponding value was $207 \cdot 184$. The Japanese material, evidently, contained very little isotopic lead.

Tin.—In two papers, Brauner and Krepelka (*ibid.*, 917, 928) give new determinations of the atomic weight of tin based upon analyses of the tetrabromide. In the first paper, which is preliminary, they find $Sn = 118 \cdot 70$. In the second, by Krepelka alone, the value $Sn = 118 \cdot 699$. This confirms the earlier determinations by Briscoe and by Baxter and Starkweather. The work of the last-named chemists appears in full in the same number of the Journal. It was noticed in our last report from a preliminary publication.

Tellurium.—From analyses of the hydride, TeH_2, Bruylants and Michielsen (*Bull. Acad. roy. Belg.*, 1919, Nos. 2—3, 119) find for tellurium the values $Te = 127 \cdot 73$, $127 \cdot 79$, and $127 \cdot 4$. The last value they reject. As these determinations are preliminary, they need no further consideration now.

Scandium.—Meyer and Schweig (*Zeitsch. anorg. Chem.*, 1919, **108**, 303), after a study of methods for the purification of their material, give determinations of the atomic weight of scandium by the usual sulphate method. They found $Sc = 45 \cdot 03$—$45 \cdot 37$, in mean $45 \cdot 23$, but conclude that the method is untrustworthy. Hönig-schmid (*Zeitsch. Elektrochem.*, 1919, **25**, 93), with some of the same material, prepared scandium bromide and determined its ratio to silver. In eighteen concordant analyses, he found $Sc = 45 \cdot 09$, which may be rounded off to $45 \cdot 1$. This value is accepted by Meyer and Schweig, and should be adopted.

Samarium.—The atomic weight of samarium has been determined by Owens, Balke, and Kremers (*J. Amer. Chem. Soc.*, 1920, **42**, 515) by analyses of the anhydrous chloride. From the mean of eighteen concordant analyses, $Sa = 150 \cdot 43$, in close agreement with

the determinations by Stewart and James, 150·44, which was noticed in our report of last year.

Apart from the actual determination of atomic weights, three papers relative to the reduction of the experimental data deserve attention. Guye (*J. Chim. Phys.*, 1919, **17**, 171), in one paper, has discussed the application of Avogadro's law to this problem. In a second paper (*ibid.*, 141), he has examined the data relative to bromine and silver, and concludes that Br=79·92 and Ag=107·87. The last figure differs from the value 107·88, as given in the table, by only 0·01, which is quite within the limits of experimental uncertainty. The third paper, by Van Laar (*ibid.*, 266), relates to the method of calculating atomic weights.

The only change in the table of atomic weights is in the case of scandium—from 44·1 to 45·1—which appears to be fully justified by the evidence.

(*Signed*) F. W. CLARKE.
T. E. THORPE.
G. URBAIN.

1921.

International Atomic Weights.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·9	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·008
Boron	B	10·9	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·005	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·1	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	45·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	70·1	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·15
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·2
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·20	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	173·5
Lutecium	Lu	175·0	Yttrium	Yt	89·33
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

C.—Organic Derivatives of Tellurium. Part II. Constitution of the Dimethyltelluronium Dihaloids.

By RICHARD HENRY VERNON.

IN Part I. (this vol., p. 86), the isomerism of the dimethyltelluronium dihaloids of the type $TeMe_2X_2$ was established.

It was likewise shown that there were two bases, the a and the β, and that the latter was obtained by evaporating (under specified conditions) an aqueous solution of the former to complete dryness.

Direct analyses of pure samples of the β-base have confirmed the supposition that it was dimethyltelluronium oxide, $TeMe_2O$.

Analysis of the a-base is out of the question, since investigation has shown that it can only exist as such in the presence of an excess of water. If this excess is gradually removed by evaporation, there is a gradual transition from the a- to the β-form, and it will be proved in the experimental part that complete conversion is accompanied by the loss of water; and that, furthermore, the relationship existing between the two bases is expressed by the equation :

$$TeMe_2O + H_2O = [TeMe_2O]H_2O.$$
$$\beta\text{-Base.} \qquad\qquad a\text{-Base.}$$
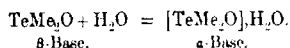
If the a-base had the indicated constitution, it would give the β-dihaloids on treatment with halogen acids and not the a. It must, therefore, be a dimethyltelluronium dihydroxide, $TeMe_2(OH)_2$.

That two bases, $TeMe_2O$ and $TeMe_2(OH)_2$, give totally different isomeric halogen derivatives can be explained by assuming that the radicles in the two bases are differently arranged around the tellurium atom, and since in the β-base two valencies of the tellurium are directly connected with an oxygen atom, it is reasonable to suppose that the corresponding haloids have the halogens (and hence the methyl groups) in proximity to each other.

In short, the β-dihaloids have a *cis*-constitution, and the above hypothesis leads to a *trans*-constitution for the a.

The constitution of the two bases is therefore

a-Base. β-Base.
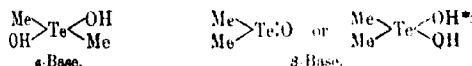
and that of the corresponding dihaloids

a-Dihaloid. β-Dihaloid.
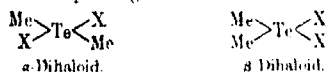
* It is quite immaterial whether the β-base be written as a dihydroxide, $TeMe_2(OH)_2$, or as the oxide, $TeMe_2O$, provided its cis-constitution is indicated.

Some interesting observations were made during the investigation of methyl telluride, which was prepared for the first time in a state of purity.

The position of the methyl groups in methyl telluride must be the same as their position in the α-dihaloids because methyl telluride directly unites with the halogens according to the equation

$$TeMe_2 + X_2 = TeMe_2X_2,$$
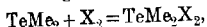
giving the corresponding α-dihaloids but never the β.

According to the extent of oxidation of methyl telluride with hydrogen peroxide, either the α- or the β-base can be obtained.

The α-base can be directly oxidised to *dimethyltellurone*, $TeMe_2O_2$, through the intermediary of the β-base, and another intimate relationship existing between these substances can be expressed by the scheme :

$$\begin{array}{l} \dfrac{Me}{OH}{>}Te{<}{OH \atop Me} \longrightarrow \text{ α-dihaloids.} \\[2mm] TeMe_2 \longrightarrow \dfrac{Me}{Me}{>}Te{<}{OH \atop OH} \\[2mm] \dfrac{Me}{Me}{>}Te{\ll}{O \atop O} \end{array} \right\} \longrightarrow \text{ β-dihaloids.}$$
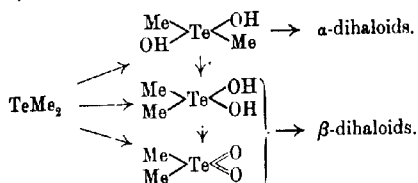
As is to be expected, the tellurone also gives β-dihaloids with halogen acids.

Since methyl telluride can be obtained by the dry distillation of either the α-* or β-base, by reduction of an α-dihaloid, or from a β-dihaloid by conversion into the base and subsequent dry distillation of the latter, there exists a regular reversible cycle between the two bases and methyl telluride.

$$TeMe_2 \; {\rightleftharpoons} \; \begin{array}{l} \dfrac{Me}{OH}{>}Te{<}{OH \atop Me} \\[2mm] \downarrow \\[1mm] \dfrac{Me}{Me}{>}Te{<}{OH \atop OH} \end{array}.$$
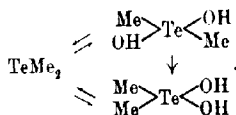
The direct transition from the β- to the α-base is, however, not possible.

●Dry distillation of either an α- or a β-dihaloid always gives tellurium and the corresponding methyl haloid, according to the equation :

$$TeMe_2X_2 = Te + 2MeX,$$

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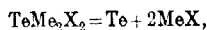
* It should be noted that the α-base consists of the β-base plus water, $TeMe_2(OH)_2 = TeMe_2O + H_2O$; hence if the β-base gives methyl telluride on dry distillation, so does the α.

and, although but little insight into the constitution of these substances is gained, the experiment indicates (but does not establish) the equivalence of the four tellurium valencies. If the four valencies were not equivalent, the dry distillation of one series of dihaloids would probably give different products of decomposition from that of the other.

The most remarkable difference between the α- and the β-dihaloids is their behaviour towards alkali hydroxides or carbonates. Thus the α-di-iodide and potassium carbonate give di-iodotetramethylditelluronium oxide, $Te_2Me_4I_2O$.

$$\underset{I}{\overset{Me}{}}\!\!Te\!\!\underset{Me}{\overset{I}{}} + \underset{Me}{\overset{I}{}}\!\!Te\!\!\underset{I}{\overset{Me}{}} + K_2CO_3 \longrightarrow$$

$$\underset{I}{\overset{Me}{}}\!\!Te\!\!\underset{Me}{\overset{--O--}{}}\underset{Me}{\overset{}{}}\!\!Te\!\!\underset{I}{\overset{Me}{}}.$$
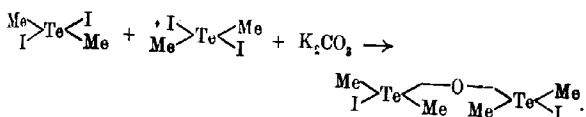
On the other hand, the β-di-iodide and potassium carbonate give trimethyltelluronium iodide, $TeMe_3I$.

Since trimethyltelluronium iodide can also be prepared from the α-di-iodide, it follows that both α- and β-dihaloids give the same trimethyltelluronium haloids. The *cis*-position of the methyl radicles in the β-dihaloids militates against their stability, and they are inclined to wander. This has been observed repeatedly, and is in marked contrast to the great stability of the methyl groups in α-derivatives. No wandering of methyl groups in an α-dihaloid has ever been noticed.

The wandering and general instability of the methyl groups in the β-dihaloids has made it impossible to prepare other derivatives than the dihaloids.

Normal salts of the α-series can be prepared in any number and without the slightest difficulty. As an example, the α-benzoate prepared by the interaction of the α-di-iodide and silver benzoate has already been mentioned in Part I. All attempts to prepare the corresponding β-benzoate resulted in an amorphous powder of indeterminate composition.

The general behaviour of the β-dihaloids indicates that the *cis*-position of the methyl groups is not conducive to their stability, and the whole molecule appears to be in a state of strain. The *trans*-position is the normal and stable one, as is evident by the perfectly normal behaviour of the α-series.

The designation of the two series by the letters α and β will be adhered to, since these prefixes are simpler than "cis" and "trans," and the dimethyltelluronium dihaloids, considered as a whole, will be referred to as "dihaloids" or "haloids" for short.

L L*

EXPERIMENTAL.

Methyl Telluride.

The first mention in the literature of methyl telluride, $TeMe_2$, is by Wöhler and Dean (*Annalen*, 1855, **93**, 233), who obtained a dark brown oil by the action of barium methyl sulphate on potassium telluride.

This oil was not investigated as such, but the conclusion that it was methyl telluride was drawn from indirect evidence; for on treatment with nitric acid, the nitrate, to which was assigned the formula $TeMe_2O,2HNO_3$, gave with halogen acids the haloid derivatives. Wöhler and Dean also mention that the oil in question boils below 100°, and that it is heavier than water, but not miscible with it.

Attempts to prepare methyl telluride by this method invariably gave a black tarry mass, and although the nitrate, and hence the haloids, could be obtained, methyl telluride as such could not be isolated.

Another experiment, using methyl sulphate and potassium telluride, gave an oil containing sulphur which was not further investigated. The interaction between methyl iodide and potassium telluride gave a negative result.

It was at length found that methyl telluride could be prepared by the reduction of Demarçay's iodide with sodium sulphite in the presence of sodium carbonate. Other reducing agents invariably reduced the di-iodide to tellurium.

An excellent yield of methyl telluride is obtained according to the equation:

$$TeMe_2I_2 + H_2O + Na_2SO_3 = Na_2SO_4 + 2HI + TeMe_2,$$
(a.)
$$2HI + Na_2CO_3 = 2NaI + CO_2 + H_2O.$$
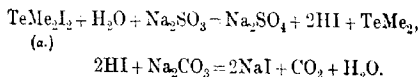
To a solution of 13 grams of sodium sulphite (hydrated) and 6 grams of sodium carbonate in 200 c.c. of water contained in a 500 c.c. distilling flask connected with a long, water-cooled condenser, 20 grams of the α-iodide are added. The flask is gently warmed, the iodide rapidly dissolved, and an emulsion results. The temperature is slowly raised and the telluride passes over rapidly at about 75°; most of it will have distilled over before the solution begins to boil. A few minutes' boiling will suffice.

The pale yellow or brown oil is separated from water, kept overnight with anhydrous sodium sulphate, and fractionated, when it distils at 94°/770 mm.

Methyl telluride is a very pale yellow oil which solidifies in liquid air, but not in carbon dioxide and ether, is somewhat heavier than water, and possesses the most abominable and persistent odour of all tellurium compounds (Found: $C = 15\cdot22$; $H = 3\cdot85$. Calc.: $C = 15\cdot24$; $H = 3\cdot80$ per cent.). The boiling point of methyl telluride completes the list of boiling points of the dimethyl derivatives of the sixth group of the periodic system. These are: Me_2O $-23°$, Me_2S $37°$, Me_2Se $58°$, and Me_2Te $94°$.

Methyl telluride dissolves slowly in water, and the aqueous solution does not contain the telluride as such, but is a solution of the a-base. This is shown by its alkalinity and the potassium iodide test.* The reaction between the telluride and water is probably $TeMe_2 + H_2O + O = TeMe_2(OH)_2$, the oxygen being derived from the atmosphere.

If hydrochloric acid is added to an emulsion of the telluride in water, the solution gives a positive a-iodide test, the red precipitate increasing on keeping, and being especially noticeable on the surface of the liquid, where contact with the air is maintained. The addition of a trace of an oxidising agent, such as potassium permanganate, sodium hypochlorite, etc., instantly precipitates the whole of the a-iodide. This reaction is simply due to the oxidation of the methyl telluride to the a-base, which, in its turn, gives the a-dihaloid.

The action of oxidising agents, and especially of hydrogen peroxide, is of interest, since either base, and in consequence either a- or β-haloids can be obtained.

If just sufficient hydrogen peroxide is added completely to dissolve the telluride on slightly warming, an alkaline solution is obtained which gives the usual tests for the a-base.

$$TeMe_2 + H_2O_2 = TeMe_2(OH)_2.$$
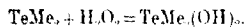
If an excess of hydrogen peroxide is used, and the solution boiled for a short time, the telluride is oxidised to the β-base, from which the β-dihaloid can be prepared.
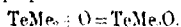
$$TeMe_2 + O = TeMe_2O.$$

Prolonged boiling of the telluride with an excess of peroxide eventually produces a turbidity and a gradual precipitation of a pure white, amorphous powder. This, as will be shown, is the thurone, $TeMe_2 + O_2 = TeMe_2O_2$.

A confirmation of these results consists in directly oxidising pre-

* A simple test to distinguish the two bases is to acidify them with hydrochloric acid, and then add a concentrated solution of potassium iodide. The a-base is indicated by a bright yellow precipitate which rapidly becomes brick-red (a-di-iodide). The β-base instantly gives a deep blood-red precipitate (β-di-iodide) without the preliminary yellow phase.

parations of the two bases, the tellurone resulting in each case.

. The action of sodium hypochlorite on the telluride is similar to the combined action of hydrogen peroxide and hydrochloric acid. Either α- or β-dichlorides are obtained.

An acid solution of potassium permanganate probably acts in the same way, and the vapour of methyl telluride is completely absorbed by a bubbler containing a 5 per cent. solution.

A fairly delicate test for the presence of methyl telluride vapour is to bubble it through concentrated sulphuric acid. This at first becomes a delicate pink, but is subsequently decolorised.

Methyl telluride deposits colourless crystals on keeping, and, although their composition is not known, they are probably some oxidation product of the telluride (β-base ?).

Dimethyltellurone.

As already mentioned, the tellurone can be obtained by oxidation either of methyl telluride, or of either of the two bases.

The best method of preparing the tellurone is to evaporate on the water-bath a solution of the α-base with an excess of hydrogen peroxide. The oxidation of the α-base appears to take place more readily than that of the β-base, but it is quite immaterial which is used. The white, amorphous powder is collected, washed with water and alcohol, and then dried. On account of its insolubility in all solvents, it cannot be further purified, and the analytical figures are not in close agreement. (Found: $C = 10\cdot50$; $H = 3\cdot19$. $C_2H_6O_2Te$ requires $C = 12\cdot60$; $H = 3\cdot20$ per cent.) This substance possesses all the characteristics of the peroxides; thus it oxidises the halogen acids to the corresponding halogen, decolorises potassium permanganate, and has explosive properties.

Trimethyltelluronium Iodide.

Trimethyltelluronium haloids, $TeMe_3X$, were first mentioned by Cahours (*Compt. rend.*, 1865, **60**, 624), and later on Scott describes the preparation of trimethyltelluronium iodide from the α- or Demarçay's iodide (P., 1904, **20**, 157).

. Trimethyltelluronium iodide is of great interest from a theoretical point of view, since it can be prepared directly from either of the two di-iodides.

Its preparation from the α-di-iodide consists in reducing the latter and then treating the methyl telluride with methyl iodide. The reaction is violent, heat is evolved, and it is advisable to dilute the telluride with some solvent like chloroform, etc. On gently

warming, the colourless, crystalline iodide is deposited. Scott prepared it directly by treating the α-di-iodide with sodium sulphite and methyl iodide.

Trimethyltelluronium iodide crystallises in colourless, fibrous needles. It has no definite melting point, and decomposes on heating. It is very readily soluble in water, and crystallises well from this solvent. (Found: $I = 42·20$. Calc.: $I = 42·40$ per cent.)

To prepare the compound from the β-di-iodide, it is only necessary to boil two molecular proportions of the latter with one molecular proportion of a concentrated aqueous solution of sodium carbonate. The colourless solution deposits the fibrous crystals on cooling, and these are recrystallised from water until their solution no longer gives a red precipitate with hydrochloric acid.

Although the mechanism of the formation of trimethyltelluronium iodide from the β-di-iodide is not clear, the obvious wandering of the methyl groups is somewhat reminiscent of the sulphonium compounds.

No explanation of this reaction will be attempted, but in view of its curious and unexpected nature, the salt was analysed. (Found: $C = 12·03$; $H = 3·14$; $I = 42·34$. Calc.: $C = 12·00$; $H = 3·00$; $I = 42·40$ per cent.)

If a methyl-alcoholic solution of the β-di-iodide is titrated until decolorisation with, for example, sodium hydroxide, one molecule of alkali is required for one molecule of the iodide (Found: 100 grams required 9·13 NaOH. Calc.: 9·73 grams).

With an alkali carbonate, one molecule is required for two of the iodide (Found: 100 grams required 12·15 Na_2CO_3. Calc.: 12·89 grams). This experiment indicated, therefore, the ratio of sodium carbonate to β-di-iodide necessary for the above preparation.

The totally different behaviour of the α-iodide towards the alkalis will be dealt with in a separate paper.

The β-Base.

Owing to the extremely hygroscopic nature of this base and its complete decomposition at relatively low temperatures, considerable difficulty attended the preparation of a pure specimen for analytical purposes. The following method was eventually adopted.

The discoloured base obtained from 24 grams of the α-di-iodide *oc. cit.*, p. 93) is redissolved in water, and the solution, after filtration, is evaporated to dryness at a temperature not exceeding $0°$ (10—20 mm. pressure), and this operation is repeated until a colourless preparation is obtained.

A boat containing the base is placed in a small weighing bottle with a ground glass stopper. This is held in a glass tube, closed

at one end, and connecting at the other through a set of calcium chloride tubes to a good water-pump. A bath containing boiling chloroform keeps the base at a constant temperature. After about ten hours, the weighing bottle is removed, weighed, and the boat instantly transferred to the combustion tube. The base cannot be dried to constant weight as it is slightly volatile (Found: $C = 13\cdot26$; $H = 3\cdot45$. Calc.: $C = 13\cdot83$; $H = 3\cdot46$ per cent.).

Distillation of the β-Base.—On heating, the base begins to decompose at about 100° at atmospheric pressure, and at 80—90° under diminished pressure.

The apparatus used in these experiments consisted of a 50 c.c. distilling flask connected to a suitably constructed receiver. The flask was heated by a sulphuric acid-bath, and the receiver was thoroughly cooled in a mixture of carbon dioxide and ether. On slowly raising the temperature, the base melts, swells enormously to a dry, powdery, brown mass, and a liquid condenses in the receiver. As a rule, the residue remaining in the distilling flask amounts to about 45 per cent. and the distillate to about 51 per cent. of the weight of base taken.

As the weight of the residue plus the weight of the distillate was never exactly equal to the weight of the base, it became necessary to ascertain whether this was due to experimental error or to some gas that was evolved during the distillation.

That the latter is not the case was shown by connecting the receiver with a eudiometer filled with mercury, and after completion of the distillation it was found that the volume of gas collected corresponded very exactly with the calculated volume of air displaced. This was confirmed by connecting the receiver through a complicated set of drying tubes with a combustion tube filled with copper oxide and kept at a red heat. No evidence of the formation of carbon dioxide or water was obtained.

Analysis of the brown residue remaining in the distilling flask showed it to be of somewhat indefinite composition. Analytical figures approximated fairly closely, however, with a compound or mixture of the type $Te_2Me_2O_2$ (Found: $C = 7\cdot60$; $H = 1\cdot92$. Calc.: $C = 7\cdot56$; $H = 1\cdot80$ per cent.).

The distillate, which passes over at about 86° under normal pressure, usually, but not invariably, consists of two layers, which are still liquid in carbon dioxide and ether. On drying this obvious mixture with anhydrous sodium sulphate, and fractionating, the upper and colourless layer passes over at 62°, and the lower and faintly yellow layer at 94°. The boiling point of 94°, and analysis of the trimethyltelluronium iodide obtained with methyl iodide, showed that this fraction was methyl telluride.

The first fraction was not further investigated, owing to the intolerable nature of these substances.

There is good reason to presume, however, that it is dimethyltelluronium dimethoxide, $TeMe_2(OMe)_2$, and the decomposition of the base on dry distillation could be expressed somewhat as follows:

$$4TeMe_2O = TeMe_2 + TeMe_2(OMe)_2 + Te_2Me_2O_2.$$
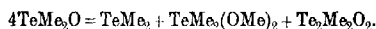
The α-Base.

If an aqueous solution of the α-base is slowly evaporated on a water-bath or in a vacuum desiccator, potassium iodide tests taken at intervals show the unaltered α-base until a certain point is reached. If the evaporation is continued still further, the presence of the β-base is at once observed.

The point at which the α- begins to change into the β-base occurs when colourless, deliquescent crystals make their first appearance in the solution.

The loss of water between the point of transition and complete conversion of the α- into the β-base corresponds closely with one molecule, and in consequence the α-base must be dimethyltelluronium dihydroxide, $TeMe_2(OH)_2$.

The composition of the α-base was determined as follows: 5·6350 grams of a somewhat syrupy solution of the base were placed in a weighed U-tube, one limb of which was sealed and the other connected with a calcium chloride tube. This in its turn communicated through a set of drying tubes to a good water-pump.

The dehydration of the syrup was effected at 70° (boiling chloroform) under 12 mm. pressure.

Potassium iodide tests were taken every hour, and the first indication of the β-base occurred after an interval of six hours, the weight of α-base and water being reduced from 5·6350 to 2·6886 grams. The calcium chloride tube was then weighed, and the dehydration continued until its weight remained constant. The crease in weight was 0·2342 gram, and the residue (β-base) in the U-tube weighed 2·3988 grams. Hence 100 grams of the α-base use 8·7 grams of water, leaving 89 grams of the β-base.

The equation $TeMe_2(OH)_2 = TeMe_2O + H_2O$ requires 9·2 grams of water and 90·8 grams of the β-base.

In view of experimental difficulties, the agreement is reasonably good.

Dry Distillation of the α- and β-Dihaloids.

A dry distillation of the β-di-iodide, conducted in precisely the same manner as that of the α-di-iodide (loc. cit., p. 91), gave

MeI $=66$; Te $=34$ (Calc.: MeI $=69$; Te $=31$ per cent.). A similar experiment with the β-dibromide gave MeBr $=58$; Te $=42$ (Calc.: MeBr $=59$; Te $=41$ per cent.).

An experiment showing the decomposition of any one of the six dihaloids, according to the general equation

$$\text{TeMe}_2\text{X}_2 = \text{Te} + 2\text{MeX}$$
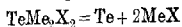
can be made by sealing up the dihaloid in a small glass tube, one end of which is drawn out into a fine point. The tube is then bent at right angles, and the dihaloid in the rounded end carefully heated. The liquid methyl haloid will condense in the pointed end of the tube, and amorphous tellurium will be found in the other.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CI.—*Volumetric Estimation of βββ'-Dichloroethyl Sulphide.*

By WILLIAM FRANCIS HOLLELY.

THE usual procedure for the estimation of $\beta\beta'$-dichloroethyl sulphide in "mustard gas" is to distil a known volume of the sample under diminished pressure and to collect the fraction boiling at 125—130°/40 mm. This product is fairly pure $\beta\beta'$-dichloroethyl sulphide, melting at about 10°, and the volume obtained affords an approximation of the purity of the crude product.

This procedure involves personal risks, and gives no accurate figure for the absolute percentage of $\beta\beta'$-dichloroethyl sulphide, as the latter fraction also contains higher chlorinated compounds and other impurities.

With the object of overcoming these difficulties, the following volumetric method for the estimation of $\beta\beta'$-dichloroethyl sulphide in "mustard gas," with or without solvents, has been devised; it depends on the fact that $\beta\beta'$-dichloroethyl sulphide forms a definite double salt with cuprous chloride, of the constitution,

$$[(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}]_2\text{Cu}_2\text{Cl}_2.$$
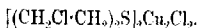
As the higher chlorinated compounds do not react with cuprous chloride, the method is applicable for the absolute estimation of $\beta\beta'$-dichloroethyl sulphide.

Procedure.—About 1 gram of the sample is weighed into a stoppered 100 c.c. conical flask, and to this 10 c.c. of a standardised solution of cuprous chloride in absolute alcoholic hydrogen chloride is added from a burette.

The cuprous chloride solution should only be prepared immediately before use. The best means to adopt is to have a 10 per cent. solution of hydrogen chloride in absolute alcohol on hand, and to dissolve 5 grams of pure cuprous chloride in 50 c.c. of it when required.

The "mustard gas" sample readily dissolves in the alcoholic solution, and the contents of the flask are allowed to remain for ten minutes in the cold, with occasional rotation. At the end of this time, the whole is gradually diluted with careful agitation and cooling in water, by the addition of 50 c.c. of a 5 per cent. aqueous sodium chloride solution from a burette.

After the addition of about 3 c.c. of the diluent, the contents of the flask become semi-solid owing to the partial precipitation of the cuprous chloride double salt, in the form of fine colourless needles; it is advisable to allow this to occur as it hastens the complete precipitation of the double salt in a crystalline condition on total dilution, whilst the excess of cuprous chloride is held in solution by the sodium chloride.

On total dilution, the contents of the flask are well mixed by careful shaking, allowed to remain for a minute or two, and the liquid is then filtered from the precipitate through glass wool into a dry burette. The filtrate is quite clear, and the amount of copper in a known volume of it is subsequently determined in terms of c.c. of $N/10$-sodium thiosulphate, by the titration of iodine liberated from potassium iodide.

It is impracticable to wash the double salt free from the excess of cuprous chloride, as it dissociates to some extent in contact with water. This difficulty is overcome by knowing the total volume of the 10 c.c. of standard cuprous chloride solution, plus the 50 c.c. of diluent, which is found to be 59·5 c.c. By this means the total excess of cuprous chloride is readily calculated from the amount contained in the known volume of the filtrate taken for the copper estimation.

Estimation of the Copper.—Usually 30 c.c. of the filtrate are run from the burette into a 250 c.c. conical flask and 5 c.c. of hydrogen peroxide (20 per cent. by volume) are added while cold to oxidise the copper to the cupric form. The contents of the flask are then gently boiled nearly to dryness, which operation is repeated twice after the addition of 10 c.c. of water to ensure that traces of gaseous oxidising agents are removed. The residue is

diluted with 50 c.c. of water and sodium carbonate solution added to give a slight precipitate, which is redissolved by the careful addition of dilute acetic acid. A slight excess of potassium iodide is added, and the liberated iodine is titrated in the usual way with $N/10$-sodium thiosulphate. Together with this, the original alcoholic cuprous chloride solution is standardised in terms of c.c. of $N/10$-thiosulphate by oxidising 5 or 10 c.c. with hydrogen peroxide, and subsequently treating as already detailed.

From the results of these titrations, the percentage of $\beta\beta'$-dichloroethyl sulphide is readily determined.

The formula of the double salt being $[(CH_2Cl \cdot CH_2)_2S]_2Cu_2Cl_2$, 127 grams of copper correspond with 318 grams of $\beta\beta'$-dichloroethyl sulphide. As 1 c.c. of $N/10$-thiosulphate corresponds with 0·00635 gram of copper, therefore 1 c.c. of $N/10$-thiosulphate = 0·0159 gram of $\beta\beta'$-dichloroethyl sulphide, the percentage of which

$$= \frac{(A-B) \times 0·0159 \times 100}{\text{Weight of sample}}, \quad \text{where} \quad A = \text{c.c. of } N/10\text{-thiosulphate}$$

corresponding with copper in the 10 c.c. of standard cuprous chloride solution, and $B =$ c.c. of $N/10$-thiosulphate corresponding with copper in the 59·5 c.c. of filtrate, that is, the total excess of copper.

The following table gives some results obtained with different samples of "mustard gas" compared with those given by the distillation method:

Sample.	Weight taken. Grams.	C.c. of $N/10$-thiosulphate. A.	B.	$\beta\beta'$-Dichloroethyl sulphide, Per cent. Titration.	Distillation.
I.............	0·9908	101·2	39·5	99·0	
	0·9617	100·2	40·4	98·5	100
	0·9032	100·2	44·0	98·9	
II.............	1·3000	127·0	49·2	95·1	
	1·0822	106·4	41·6	95·2	100
III.	1·2824	99·0	42·40	70·2	
	1·3398	99·0	40·4	69·6	76
IV.............	1·2642	99·0	49·6	62·1	
	0·9166	106·4	70·8	61·7	65

Sample I was specially pure $\beta\beta'$-dichloroethyl sulphide, obtained after three redistillations, freezing, and draining off the residual liquid. It melted at 13·5°.

Sample II.—Once distilled $\beta\beta'$-dichloroethyl sulphide from crude product. M. p. 12·5°.

Sample III.—Crude product as manufactured. M. p. 8°.

Sample IV.—Crude product + solvent. M. p. ~3°.

Higher Chlorinated Compounds and Cuprous Chloride.

Equal volumes of 95 per cent. $\beta\beta'$-dichloroethyl sulphide and sulphur monochloride were mixed and allowed to remain at the ordinary temperature for two weeks. Hydrogen chloride was evolved and sulphur separated, showing that some chlorination had taken place. The product was then distilled, no sulphur mono-chloride being obtained, and the fraction boiling at 118—120°/ 20 mm. was reserved. This fraction did not freeze even at $-7°$; therefore, the greater proportion of the fraction is composed of higher chloro-compounds, although undoubtedly some $\beta\beta'$-dichloro-ethyl sulphide was present owing to the difficulty of separating it by fractional distillation.

The following results were obtained by the volumetric method:

(a) 1·3172 Grams, using 10 c.c. of alcoholic cuprous chloride ($=102$ c.c. of $N/10$-thiosulphate), required 67·8 c.c. of $N/10$-thio-sulphate for total excess copper. Percentage of $\beta\beta'$-dichloroethyl sulphide $= \dfrac{34\cdot2 \times 1\cdot59}{1\cdot3172} = 41\cdot3$.

(b) 1·0804 Grams required 73·7 c.c. of $N/10$-thiosulphate for total excess copper. Percentage of $\beta\beta'$-dichloroethyl sulphide $= 41\cdot6$.

The sample, after treatment with alcoholic cuprous chloride and dilution, was precipitated as an oily layer, instead of the usual crystalline precipitate. This oily layer, on keeping, gradually became pasty, owing to the separation from its solution of some of the $\beta\beta'$-dichloroethyl sulphide–cuprous chloride double salt. This qualitative observation, together with the above results which show a fall in the percentage of $\beta\beta'$-dichloroethyl sulphide from 95 to 41 per cent. after chlorination, indicate that the higher chloro-compounds of ethyl sulphide do not enter into the reaction during this volumetric estimation, no copper salts of these com-pounds being formed.

Analysis and Properties of the $\beta\beta'$-Dichloroethyl Sulphide–Cuprous Chloride Double Salt.

The salt was prepared by the method already described, washed with alcohol, and dried in a vacuum, when colourless needles were obtained.

A known weight of the sample was carefully heated with a little concentrated nitric acid to dryness, a few c.c. of water were added, and evaporated. The copper was estimated as usual by potassium iodide and $N/10$-thiosulphate (Found: Cu 24·3, 24·1. $C_4H_{10}Cl_2S_2Cu_2$ requires Cu $= 24\cdot6$ per cent.).

The double salt can be obtained by a variety of means; for example, by stirring the dry components together followed by alcoholic extraction; by shaking the liquid with cuprous chloride solution in dilute hydrochloric acid, and also by the method employed in its detailed estimation. This method is by far the preferable, as it gives a quantitative yield of a crystalline product. The salt readily dissociates on warming with ether, carbon tetrachloride, etc., but less readily in alcohol, when cuprous chloride is precipitated. When heated in water, it readily melts, but dissociation is not rapid, and the salt is insoluble. When stirred with cold ammonium chloride solution or concentrated hydrochloric acid, the salt becomes pasty, owing to partial dissociation and solution of cuprous chloride in the liquid, leaving a proportion of the liquid dichloro-compound.

The crystals have a dissociation or decomposition point rather than a melting point, which occurs at about 60°.

The solubility in various solvents is difficult to judge, owing to the more or less rapid dissociation. The salt can, however, be crystallised from hot alcohol, in which it is fairly soluble, separating in colourless needles, but the solution has to be filtered from some dissociated cuprous chloride.

The vesicant power of the salt appears to be of the same degree as $\beta\beta'$-dichloroethyl sulphide itself.

General Remarks.—In the estimation of the crude product, with or without solvent, owing to the presence of higher chloro-compounds or solvent, the salt, on being precipitated from the alcoholic solution, contains some lumpy particles, due to the precipitated oily higher chloro-compounds or solvent dissolving some of the double salt. It has been proved quantitatively that these small lumps do not retain any unused cuprous chloride which should pass into solution with the sodium chloride, and the result is not affected.

This volumetric method for the estimation of $\beta\beta'$-dichloroethyl sulphide has distinct advantages over the distillation method, which does not yield $\beta\beta'$-dichloroethyl sulphide free from impurities, in that it is a much cleaner process and the personal risk is almost entirely eliminated. Moreover, it is a quick method, as an estimation can be done in less than an hour.

CII.—The Ignition of Gases. Part I. Ignition by the Impulsive Electrical Discharge. Mixtures of Methane and Air.

By RICHARD VERNON WHEELER.

THE research to which the present paper forms an introduction originated in a desire to obtain information regarding the mechanism of ignition, particularly by electrical means, of mixtures of methane and air. For it is necessary to know with certainty the conditions under which ignition of such mixtures is to be apprehended in coal-mining practice.

As the work progressed, it became apparent that the information required could not be obtained if attention was confined to methane as the inflammable gas in admixture with air, but that it would be necessary to study also the ignition of other members of the paraffin series of hydrocarbons, and of hydrogen, when mixed with air, and of methane when mixed with pure oxygen and with various mixtures of oxygen and nitrogen.

The research, so far as it has progressed, can conveniently be divided under three heads: I, Ignition by heated surfaces; II, ignition by the secondary discharge (high-tension sparks), and III, ignition by electric "break-flashes" (low-tension sparks). These can be subdivided to treat separately under heading I of: (A) Ignition by the heated walls of a containing vessel, and (B) ignition by hot wires. Under heading II can be grouped the ignition of: (A) Mixtures of methane and air; (B) mixtures of hydrogen and of different members of the paraffin series of hydrocarbons with air; (C) mixtures of methane with oxygen and with mixtures of oxygen and nitrogen. Under heading III the effects will be considered of: (A) The inductance of the circuit; (B) the rate of break of circuit; (C) the materials of the poles; and (D) the use of alternating current. It is proposed to submit separate accounts of each of these parts of the research to the Society, not necessarily in the order indicated above, as opportunity affords to prepare the results for publication.

The requisite for a source of heat to initiate flame in a gaseous mixture is that sufficient energy shall be introduced to maintain for a sufficient length of time a sufficient volume of the mixture at or above its ignition-temperature.

Sufficiency of the source of heat will depend on (a) the ignition-temperature of the mixture, and (b) the specific heats of the mixed

gases. Sufficiency of time will depend on (c) the duration of the pre-flame period for the mixture, (d) the initial speed of propagation of flame therein, and (e) its thermal conductivity. Sufficiency of volume of mixture ignited will depend on (f) the thermal value of the reaction.

It will be seen that several of these factors are interdependent. Thus, the ignition-temperature of the mixture and the duration of the pre-flame period both depend on the rate of reaction of the combining gases; whilst the initial speed of propagation of flame in the mixture also depends on the rate of reaction, as well as on its thermal value.

Although this research deals in general with the mechanism of ignition of inflammable mixtures whatever the means employed to effect that ignition, the characteristics of the igniting agent must be considered, if not completely defined. For, by the use of several kinds of igniting agents, each with different known characteristics, the importance to be attached to one or other of the many factors which determine whether or no flame shall be produced in an inflammable mixture can be gauged. Unfortunately, the amount of information available regarding the characteristics of electric discharges is very meagre.

The igniting agent employed for the series of experiments described in this paper was the high-tension spark produced at a gap in the secondary circuit of an induction coil when a current in the primary circuit was broken. When such a spark is examined in a rotating mirror or photographed on a rapidly moving film, it is found to consist of an initial bright spark followed by others of less intensity or by a striated luminous band indicating an undulatory unidirectional discharge. The initial bright spark has the characteristic appearance of a single discharge from a condenser.

According to Morgan ("Principles of Electric Spark Ignition in Internal Combustion Engines," London, 1920), the most important consideration regarding secondary discharges is that each discharge consists of two successive phases, namely, a "capacity component" and an "inductance component." The former corresponds with the spark obtained by the discharge of electrostatic energy from a condenser, the latter with the discharge of electromagnetic energy from a coil. The duration of the capacity component of the secondary discharge is always extremely short, but the value of the current reached in it is much higher than that of the current in the inductance component. The capacity component can be intensified at the expense of the inductance component by increasing the capacity associated with the spark-gap circuit, and it is then found that the igniting-power of

the spark is increased (although its total energy has not been altered). This suggests that when ignition of inflammable mixtures is caused by the secondary discharge, the effective part of that discharge is the capacity component. Paterson and Campbell (*Proc. Physical Soc.*, 1919, **31**, 193) so far share Morgan's views as to suggest that the igniting-power of the discharge is determined by the quantity of electricity in the first spark that passes.

We can, then, characterise the secondary discharge from an induction coil, in relation to its ability to ignite inflammable mixtures, as of exceedingly short duration and high intensity, assuming, with Morgan, that the "capacity component" of the discharge is the effective portion.

For an igniting source of these characteristics, the relative "ignitibilities" of mixtures of methane and air are shown in Fig. 3 (Curve *A*). In this diagram, percentages of methane, over a wide range, are plotted against "igniting-currents"; that is to say, the currents in the primary circuit of an induction coil, which, when broken at a constant rate, induced secondary discharges, at a fixed spark-gap, just capable of igniting the mixtures.

When, as in these experiments, the gap is formed by sharply pointed electrodes, and the voltage is applied with great suddenness (as is the case with an induction-coil), the sparking voltage for a gap of constant width follows, over a wide range, a straight line relationship with the primary current. The energy-content of the "capacity component" of the discharge is $\frac{1}{2}CV^2$, where C is the capacity associated with the gap circuit (including that of the secondary winding) and V is the sparking voltage. Assuming that ignition depends on the energy of the capacity component (and the best available evidence is in accordance with this assumption), it is rational to co-ordinate i^2 (primary current) with percentage of inflammable gas in the mixture. The general character of the curve will not be altered by plotting i, instead of i^2, against percentage.

For our present purpose, it is sufficient to define the induction-coil used for the experiments as an "8-inch" coil of the *X*-ray type. The "trembler" of the coil was removed and direct connexion made between the leads of the primary circuit and a battery of accumulators. Included in the circuit was a contact-breaker of the type previously described (T., 1917, **111**, 130), a regulating resistance, and a Weston A.C. ammeter. The last-named was short-circuited whenever a discharge was passed at the spark-gap, a non-inductive resistance equal to its resistance being included in the circuit in its stead. In some of the earlier series of experiments, a capacity (of 0·25 microfarad) was inserted across the

terminals of the mechanical circuit-breaker to reduce sparking on break, and thus avoid oxidation of the polished steel contacts. To obtain consistent results, it was essential that these contacts should remain clean, and, when currents of much more than 1 ampere were broken, the presence of the capacity aided considerably in maintaining their cleanliness. Duplicate experiments showed that the discharge at the spark-gap in the secondary circuit was un-affected by the capacity across the break in the primary circuit. In later experiments, when the current broken rarely exceeded 1 ampere, the capacity was removed.

The spark-gap was between platinum wires 2 mm. in diameter coated with glass to within 1 mm. of their ends, which were sharpened to fine points. These electrodes were sealed, with accurate alignment, into a glass globe of 75 c.c. capacity, so as to form a horizontal spark-gap, the globe being fitted at the top with a three-way tap (see T., 1917, **111**, 133, Fig. 2).

The mixtures of methane and air were prepared in glass gas-holders over a mixture of equal parts by volume of glycerol and water, and were analysed before use. The gas-holder containing the mixture to be experimented with was attached by means of stout rubber pressure tubing to one limb of the three-way tap on the explosion-vessel, a glass tube packed with cotton wool being interposed to serve as a filter. The other limb of the three-way tap made connexion, through a calcium chloride tower, with a vacuum pump.

The method of experiment was that of trial and error. A charge of a given mixture having been introduced into the explosion-vessel at atmospheric temperature and pressure, the current in the primary circuit was adjusted to an arbitrary value and the discharge caused to pass at the spark-gap. If ignition of the mixture occurred, the explosion-vessel was rapidly exhausted and a fresh charge allowed to enter from the gas-holder; this was allowed to remain for a few seconds, and then removed by exhaus-tion, the explosion-vessel being finally refilled.* The current in the primary circuit was now adjusted at a lower value; if the secondary discharge produced on breaking this current did not ignite the mixture during ten trials (made at intervals of about five seconds each), it was increased by 0·01 ampere, and ten further discharges were caused to pass. Eventually a value for the current in the primary circuit was found such that the secondary discharge,

* The object of this procedure was to avoid the condensation of moisture, produced by the combustion of the methane, within the explosion-vessel, and to maintain the same saturation of water-vapour in the mixtures through-out a series of experiments.

produced on breaking it at a constant rate, ignited the mixture within the first few trials, a current 0·01 ampere less in value giving, under the same conditions, a secondary discharge incapable of igniting the mixture in one hundred or more trials. The final value for the "igniting current" for a given mixture was checked by making four or five trials with fresh charges of the mixture at, and 0·01 ampere below, the current found in the preliminary trials.

If a discharge was capable of igniting a mixture, it usually did so at the first, or within the first three, trials. That it did not do so invariably at the first trial is ascribable to slight alterations in the experimental conditions, either at the contact breaker or at the spark-gap. Ordinarily, the contrast between the current necessary to produce a discharge which would, and one which would not, ignite a given mixture was very sharp, the one, as aforesaid, causing ignition within the first two or three discharges, the other, ·01 ampere less, being incapable under the same conditions of producing an igniting discharge, however often trial might be made. Occasionally, however, irregularities were observed, ignition of a given mixture perhaps occurring with the usual "igniting current" only after fifty discharges. Such an irregularity could always be traced to oxidation of the polished steel contacts of the primary circuit-breaker; on re-polishing the contacts, the irregularity disappeared. More rarely, when it was found that a much higher current than usual was unable to produce a discharge capable of igniting a given mixture, irregularity could be traced to the condition of the spark-gap; a minute speck of dust had perhaps lodged on one of the sparking-points. On such occasions, cleaning of the explosion-vessel with chromic and sulphuric acids restored the spark-gap to its original condition, a fact which was tested by trial of a "standard" mixture (8·5 per cent. of methane). As a matter of routine, the testing of this standard mixture was frequently interposed between dissimilar mixtures to give assurance that the conditions of experiment were being maintained unchanged.

I have described in some detail the precautions most necessary in carrying out work of this character, because the belief, first promulgated by Thornton (*Proc. Roy. Soc.*, 1914, [*A*], **91**, 17), that continuous alteration of the proportions of gas and air in an inflammable mixture can be accompanied by discontinuous alteration in the intensity of spark required for ignition, has recently been revived by Paterson and Campbell on their observance of an apparent discontinuity of a different kind (*loc. cit.*, p. 212).

Paterson and Campbell's observations were on the relation

between the capacity and the spark potential necessary to cause the ignition of a given gas mixture the composition of which remained the same throughout any one series of experiments. Two series of their observations are reproduced in Fig. 1, which is the authors' Fig. 9, without certain lines, intended to represent discontinuities or "steps," which they draw through the observed points. It will be seen that the results can be represented equally as well by a "smooth" as by a "stepped" curve. It does not appear from Paterson and Campbell's paper that these irregularities were invariably produced in the same positions on repeated trials (in which event they might properly be regarded as regularities, and some significance would attach to them), for the two

Fig. 1.
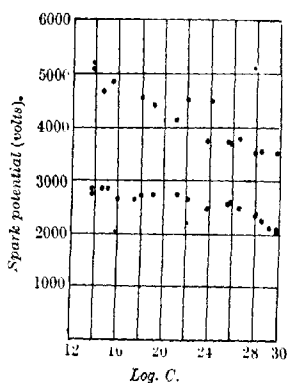
series of observations selected are stated to be unusually free from inconsistency. That being so, some unobserved lack of uniformity in the manner of carrying out the determinations would seem a reasonable explanation of the lack of uniformity of the results. At all events, it is rather far-fetched to relate, as do Paterson and Campbell, these inconsistencies in the physical characteristics of the discharge, supposing they exist, with the discontinuities in the chemical characteristics of inflammable mixtures presumed by Thornton.

Paterson and Campbell themselves obtained quite smooth curves relating the composition of different mixtures of hydrogen and air with the spark potential (of capacity sparks) required for ignition (compare Thornton, *loc. cit.*, p. 387). Their suggestion is that "the igniting-power of a spark is very much more sensitive to

changes in composition than to the capacity discharging in the spark; that is to say, a given percentage change in composition involves a very much greater percentage change of critical capacity. Accordingly, the effect of substituting as abscissa composition for capacity is much the same as diminishing very greatly the scale of abscissæ in Fig. 9, while the scale of ordinates is unchanged." This compression of the scale of abscissæ in Fig. 9 (Fig. 1 of this paper) would mask the irregularities. Hence arises "the failure of Wheeler and others to observe 'stepped ignition.' All those

FIG. 2.

Per cent. of methane in air.
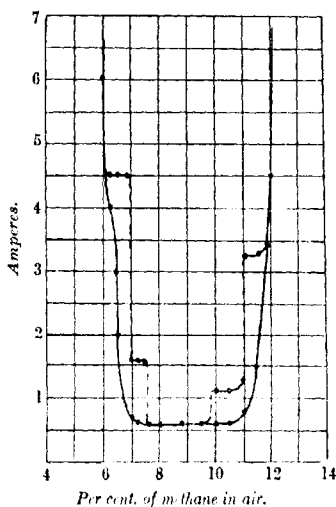
who failed used the 'induction' spark and varied intensity by means of the primary current broken. Thornton, on the other hand, varied the capacity."

It is true that in one series of experiments Thornton was concerned with the ignition of gases by condenser discharge sparks, and obtained a measure of the relative ignitibilities of certain mixtures by varying the capacity, but Paterson and Campbell ignore the fact that the most notable examples of discontinuity were recorded by Thornton when using "induction" sparks. The work of mine referred to in the sentence quoted above formed a direct check on experiments made in a similar manner by Thornton, and is so described (T., 1917, 111, 130, 411).

The example of Thornton's stepped ignition which I was unable to confirm (ignition by the impulsive discharge of a mixture of methane and air, 9·5 per cent. of methane, the pressure of which was

FIG. 3.
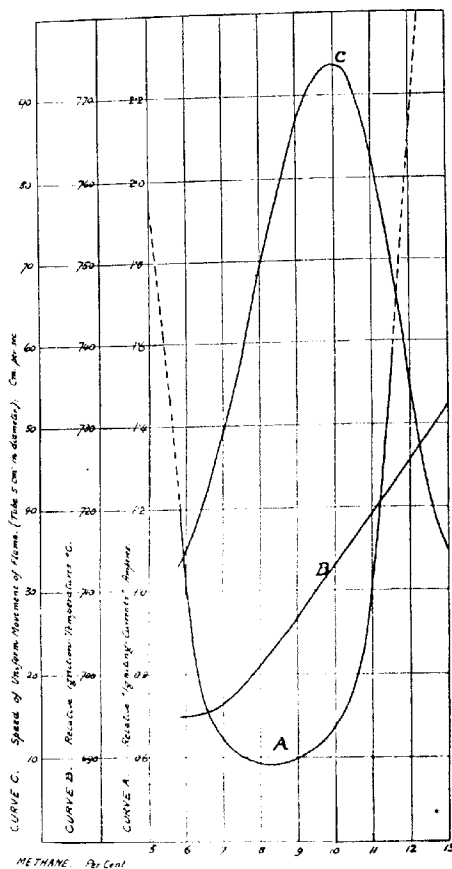
varied) was chosen as presenting few sources of error; for example, the composition of the mixture remaining unchanged, errror of analysis would not affect the results.   Moreover, the steps recorded by Thornton were remarkably well defined.   Thornton has, how-

ever, obtained a rather ill-defined stepped curve for the relation between the composition of mixtures of methane and air and their ease of ignition by the impulsive discharge, and, in view of Paterson and Campbell's suggestion, reference must be made to this work. The "stepped" curve is reproduced in Fig. 2. Thornton's comments thereon include the following (*loc. cit.*, p. 388): "With this kind of ignition methane appears to be sensitive to slight changes on the surface of the poles." "If the poles were not cleaned after every few explosions, steps occurred in the curve . . . which disappeared again when the poles were cleaned."

In other words, as was to have been expected, unless the conditions of experiment were maintained constant, discordant results were obtained. It is conceivable that all the peculiar discontinuities which have dogged Thornton's steps during his researches on the ignition of gases can be ascribed to the lack of similar precautions to that of maintaining the cleanliness of the electrodes.

Curve *A* in Fig. 3 represents the results obtained in the present research when the spark-gap was about 1 mm. in length. Four other curves have been obtained (each with between twenty and twenty-five observed points) using different explosion-vessels in which the spark-gap was also about 1 mm., and two curves for spark-gaps of about 0·5 and 3 mm. respectively. For the two last-named curves, the general experimental conditions were as for the one reproduced in Fig. 3; for the four additional curves with 1 mm. spark-gap, changes were purposely made in the experimental conditions (which were, however, maintained constant for any one series of experiments) in attempts to obtain some indication of "steps." Thus, the rate of break of the primary current, the voltage of the primary current, and the construction of the induction-coil were each altered; for two of the series (by different observers), the precaution was taken of leaving the observer in ignorance of the composition of the mixture undergoing test, lest a latent desire, if such there was, to obtain a smooth curve should unconsciously affect the care with which critical mixtures were tested. In no instance was any other than a smooth curve, comparable in every respect with that reproduced in Fig. 3, obtained.

If the current in the primary circuit of an induction-coil is maintained constant and the width of the gap in the secondary circuit is varied, a straight line relationship exists between the sparking voltage and the width of the gap, similar to that which exists, as already stated, between the primary current and the sparking voltage when the secondary gap (between sharply pointed

electrodes) is of constant width.   A check on the validity of curve A of Fig. 3 can thus be obtained by plotting g^2 (secondary gap) or g against percentage of inflammable gas, i (primary current) being maintained constant.   A series of determinations of this character was made, the electrodes being a disk of platinum 1 cm. in diameter and a sharply pointed cone of platinum attached to a micrometer head to admit of accurate measurement of the

FIG. 4.
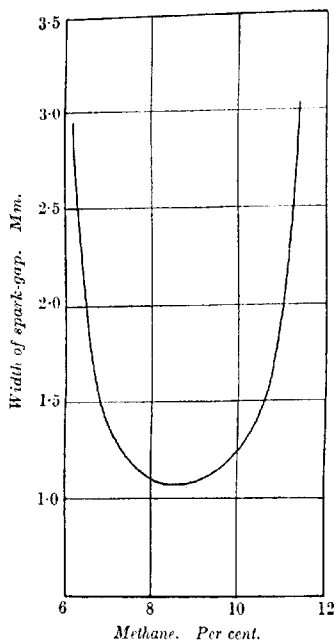
Methane.   Per cent.

width of the gap.   The current in the primary circuit was main-tained constant at 1·0 ampere.   The curve obtained when width of gap in mm. was plotted against percentage of methane is repro-duced in Fig 4.   It is identical in character with curve *A* of Fig. 3.

The characteristics of the curves (Fig. 3 [.1] and **Fig.** 4) to which attention should be directed are: (1) the greatly increased difficulty of ignition as the limits of inflammability are approached, particularly on the high limit side; and (2) the position of a range

for optimum ease of ignition between 8·2 and 8·5 per cent. methane.

It should be noted that no attempt has been made to determine the limits of inflammability of the mixtures in the course of these experiments. Such determinations would only have been significant in relation to the explosion-vessel (of 75 c.c. capacity), the size of which did not admit of judging to what extent the continued propagation of flame was possible in the mixtures.

Moreover, mixtures which can be ignited by a sufficiently intense source of heat—and it is the problem of ignition with which we are now concerned—are not necessarily capable of propagating flame any considerable distance away from that source of heat. An illustration of this is to be found in the "cap" or aureole that warns miners of the presence of firedamp in coal-mines. An aureole due to burning methane can be seen around a non-luminous oil-flame when less than 1 per cent. of the gas is present in the air, and this aureole increases in size (mainly in length) as the percentage of gas is increased, until with 5 per cent. of methane it may be many inches long. The lower limit of inflammability of methane, however, even for upward propagation of flame, is not less than 5·3 per cent. Similarly, if a sufficiently intense electric spark is caused to pass in a mixture of methane and air containing but a trace of methane, a cap may be seen above the spark, and if the quantity of methane be 4 or 5 per cent., the momentary cap may be sufficiently large to fill the explosion-vessel. This production of large caps in small explosion-vessels has misled several observers into placing on record false limits of inflammability.

It will be understood, then, that mixtures which contain less inflammable gas than is required for a lower-limit mixture (or more than is required for an upper-limit mixture) can be ignited, and it may be important to determine the relative ignitibilities of such mixtures, as will be seen when the ignition of mixtures of air with the higher members of the paraffin series is considered.

The limits of inflammability, upward propagation of flame, for mixtures of methane and air are, lower, 5·3, and upper, 14·3, per cent., and a local inflammation can be obtained in mixtures beyond those limits. The determinations of "igniting-currents" were, in general, restricted to such mixtures as required no more than 1·25 amperes. For, apart from the fact that when currents higher than this were broken in the primary circuit, the need for re-polishing the surfaces of the contact-breaker became over-frequent, the form of the secondary discharge with a 1 mm. gap changed, inasmuch as it spread back along the electrode instead of appearing exclusively from the point, as it did when the current broken

in the primary circuit was not much more than 1 ampere, so that the size, as well as the intensity, of the source of ignition changed. Igniting currents higher than 1·25 amperes therefore did not bear a strict relation to those of lower value when a spark-gap of 1 mm. was used. With a spark-gap of 3 mm., no change in the form of the discharge appeared as the current in the primary circuit was increased up to 3 amperes, and the "igniting-currents" were, over the whole range of mixtures, lower with this gap than with the 1 mm. gap, so that the true relative ease of ignition of methane–air mixtures at the lower and upper limits of inflammability could, if necessary, be determined by the use of a wider spark-gap. The fact to be emphasised is that the terminal points on Curve A in Fig. 3 do not represent the "limits" of igniting-power of the discharges for the mixtures. Despite the steep slope of the curve towards those terminal points, the range of igniting-power of the discharge extends, as already explained, beyond the limits of inflammability of the mixtures, and the curve can be extended, as shown in dotted line. On the other hand, the graph reproduced in Fig. 4 is nearly complete. For with a constant current of 1·0 ampere in the primary circuit, mixtures containing less than 6·0 or more than 11·5 per cent. of methane could not be ignited by the secondary discharge under the conditions of the experiments, whatever the width of the gap. The reason for this will be explained in a subsequent communication.

Of the factors enumerated on p. 903 as determining, in general, the ignitibility of gaseous mixtures, the thermal conductivity and the specific heat of the mixture can be regarded as of relatively little importance so far as the range of mixtures of methane and air under examination is concerned. Similarly, the voltage of the spark can be regarded as unaffected by change in the insulating power of the mixtures, which is, indeed, practically constant. (In this connexion, see Wright, T., 1917, **111**, 643.) There remains to be considered the ignition-temperatures of the mixtures, the duration of the pre-flame period, and the initial speed of propagation of flame in them, and their thermal values.

When these factors are considered in conjunction with the characteristics of the igniting-source, which are "high intensity and exceedingly short duration," it will be realised that the relative ignition-temperatures, in themselves, of the mixtures are not likely to determine whether one mixture rather than another is more easily ignitible by such a source. For it can be assumed that the temperature to which the gases in the path of any of the discharges represented by the "igniting-currents" in Fig. are raised is far in excess of the ignition-temperature of any of

the mixtures. The relative ignition-temperatures of mixtures of methane and air, when in contact with a heated surface, have been determined by Mason, whose work will be described in Part II of this research. A curve constructed from his determinations is reproduced in Fig. 3 (Curve B) for comparison with the "igniting-current" curve. The only relation between the two curves lies in the increasing difficulty in the ignition of mixtures rich in methane, or, to express the matter more significantly, poor in oxygen, disclosed by both. Any influence that the ignition-temperature of the mixtures may have on their ignition by the secondary discharge will therefore tend to cause the more ready ignition of mixtures containing an excess of oxygen.

A curve (Curve C) showing the relative speeds of propagation of flame ("uniform movement") in mixtures of methane and air over the same range is reproduced in Fig. 3 (see T., 1917, 111, 1044). This curve is, with an important difference, which is referred to later, nearly the inverse of the "igniting-current" curve. The inference is that the intensity of the secondary discharge necessary to cause the ignition of a given mixture—necessary, that is to say, to ensure that flame shall travel away from the immediate vicinity of the discharge—is mainly dependent on the initial speed with which flame can travel in that mixture.

We know that there is combination of the gases in the path of a discharge which does not cause "ignition" of an inflammable mixture. Close observation of the discharges produced in the mixtures of methane and air by currents slightly less than the igniting-currents" disclosed the fact that such discharges were accompanied by minute tongues of flame, which shot out above and below the spark-gap in the form of a V, with an inverted V above it $\left(\begin{smallmatrix}\wedge\\\vee\end{smallmatrix}\right)$. These tongues of flame were produced in all the mixtures of methane and air, but were more noticeable (because larger) in mixtures near the limits of inflammability, and most noticeable (because of the superior luminosity of the flame) near the upper limit. Moreover, with such mixtures the interval between the "igniting-current" and one which produced a discharge capable of forming these tongues of flame was greater than with the more readily ignitible mixtures.

The passage of the discharge, though it may cause the combination of the gases in its immediate vicinity, is incapable of resulting in the general ignition of a mixture unless the initial impetus it gives to the speed of propagation of flame in the mixture is sufficient to carry the flame through a sufficient volume. In amplification of this statement, I may quote from a report

prepared for the Explosions in Mines Committee of the Home
Office (H.M. Stationery Office, Cd. 6704 of 1913): "Imagine a
small sphere of hydrogen and oxygen 1 mm. in diameter at atmo-
spheric pressure heated by an electric spark: the complete com-
bustion of the gases in this sphere (the volume of which is about
0·5 cu. mm.) would yield less than the one-thousandth of a
(small) calorie of heat. In order to spread the flame, this heat
has to be communicated to the spherical shell of unburnt gas in
contact with the sphere (the surface of which is 3·1 sq. mm.) and
bring a certain thickness of that shell to its ignition-temperature.
It may fail to do so. Let us suppose that the diameter of the
heated sphere is doubled: the volume of gases fired is now eight
times as large, whilst the surface is four times as large as before.
By increasing the size (or the intensity) of the spark, a point
is soon reached at which the combustion produced by the spark
evolves enough heat to fire *per se* the adjacent gas-mixture—and
the flame is propagated."

It will be understood, from these considerations, why the ease
of ignition of an inflammable mixture by a momentary source of
heat, such as the secondary discharge, is so dependent on the
rapidity with which a sufficient volume of the mixture becomes
ignited; that is to say, on the initial speed of propagation of flame
in the mixture. This dependence, which will be shown in Part III
of this research to obtain with inflammable gases other than
methane, is not, however, complete. The mixtures of methane
and air in which the initial speed of propagation of flame is
fastest contain between 9·5 and 10·0 per cent. of methane, whilst
the mixture most easily ignitible by the secondary discharge lies
within the range 8·2 and 8·5 per cent. methane, the majority of
the determinations inclining towards a percentage of 8·3.

The lower ignition-temperatures of mixtures of methane and air
containing an excess of oxygen will, as already stated, cause them
to be more readily ignited by an intense source of heat of short
duration, and a simple explanation of the position of the range of
mixtures most easily ignitible by the secondary discharge, an
explanation which accounts also for the greatly increased difficulty
there is in igniting by such means mixtures rich in methane, is
that the curve for relative "igniting-currents" is compounded of
the relative ignition-temperature curve and the inverse of the
curve relating composition of the mixtures with initial speed of
propagation of flame therein.

EXPERIMENTAL.

The determinations from which Curve A in Fig. 3 is constructed are as follow:

Methane. Per cent.	Relative " Igniting-current." Amperes.	Methane. Per cent.	Relative " Igniting-current Amperes.
5·85	1·20	8·60	0·59
6·00	1·05	8·85	0·60
6·25	0·86	9·15	0·61
6·35	0·79	9·40	0·62
6·40	0·78	9·50	0·63
6·55	0·71	9·70	0·64
6·60	0·70	10·00	0·68
6·85	0·67	10·40	0·74
7·05	0·63	10·50	0·79
7·20	0·62	10·70	0·86
7·50	0·61	10·80	0·89
7·95	0·59	10·90	0·98
8·00	0·59	11·10	1·12
8·20	0·585	11·50	1·56

The curve in Fig. 4 is constructed from the following determinations:

Methane. Per cent.	Width of gap. Mm.	Methane. Per cent.	Width of gap. Mm.
6·20	2·94	8·90	1·09
6·50	1·95	9·45	1·13
6·95	1·39	9·90	1·23
7·40	1·22	10·50	1·42
8·05	1·10	11·05	1·98
8·30	1·08	11·35	2·75
8·50	1·08	11·40	3·02

For carrying out many of the laborious series of determinations rendered necessary by the fruitless search for "steps," I am indebted to my wife; for the numerous gas analyses required, Mr. J. Mason is responsible.

HOME OFFICE EXPERIMENTAL STATION,
ESKMEALS, CUMBERLAND.   [*Received, June 8th*, 1920.]

III.—*The Composition of Ancient Eastern Bronzes.*

By MASUMI CHIKASHIGE.

AMONG the various examples of ancient Japanese and Chinese art, the bronzes are most suitable for the purpose of examining the nature of ancient metallurgical methods. They resist the corrosive action of time much better than do other common alloys or metals

M M 2

and preserve the features of ancient art correctly. Brass articles are not so antique as bronze. They date from about the tenth century, that is, the beginning of the Sung dynasty.

As excavated objects are always covered with rust, it has been the custom to remove this before analysis. Since, however, the constituents of an alloy, which is simply a mixture, would retain their individual properties, the rate of rusting must differ in the case of each metal. In bronze, a selective corrosion takes place in the order: lead, copper, and tin. The metallic proportions in the rust will differ from those in the original alloy, becoming much enriched with copper. Montelius, in his "Chronologie der ältesten Bronzezeit," 1900, p. 151, gives the following analysis of two similar Egyptian rings:

	1.	II.
Copper	79·51	16·23
Tin	9·65	75·66

The first ring seems not to have undergone much change, but the second must have lost most of its copper by oxidation. It is obvious, therefore, that it is not correct to remove the rust and to submit what remains only to analysis.

The author's method of analysis is therefore to remove earthy matter from a rusted article and to analyse rust and metal together. This gives, of course, too low a percentage for the metallic constituents, which should therefore be recalculated for 100.

Even this method becomes objectionable in a case where the composition of the rust has undergone change by a partial solution or disintegration before analysis. This is due, not to an incorrect method, but to lack of the right samples.

Mirrors.

The ancient bronze mirrors may be divided into four classes, namely, white, pale yellow, deep yellow, and red, according to their surface colours. These differences in colour are due to the amount of tin becoming less and less, and corresponding exactly with the chronological period in which the mirrors were made. In the most recent times, zinc is employed instead of tin, giving rise to the use of brass mirrors. The mirrors belonging to the white and pale yellow class were effective without further alloy, but those belonging to the other classes, together with the brass, had necessarily to be alloyed with mercury before use. Brass as well as bronze objects with less tin are, however, more easily cast, and they were rapidly adopted, probably with the invention of amalgamation, in the East.

The following is a summary of analyses of bronze mirrors differing in ages and compositions:
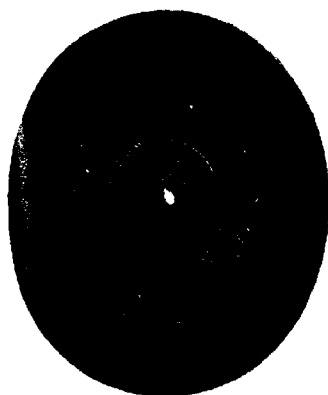
FIG. 1.
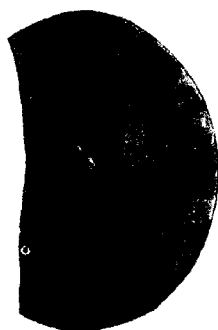
FIG. 2.
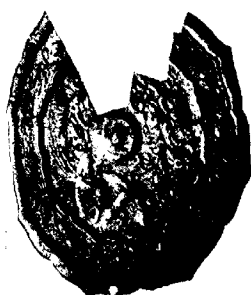
FIG. 3.

FIG. 4.
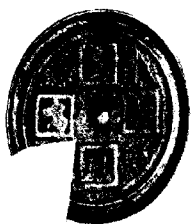
FIG. 5.

FIG. 6.
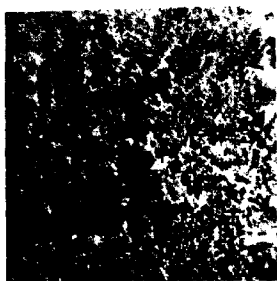
FIG. 7.

FIG. 8.

FIG. 9.
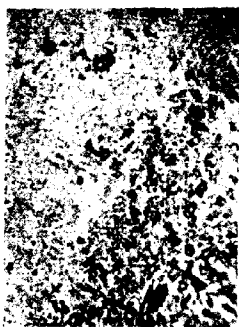
No.	Description	Colour	Fig.	Copper 65·10	Tin 25·07	Lead 9·12	Zinc 0·16	Iron 0·06	Arsenic trace	Antimony trace	Nickel	Silver	Gold	Copper to tin 72:28
1	Chinese bronze mirror. I. Cent. (Han Dyn.) ½ excav. in China			66·07	26·57	5·29	0·20	0·81	—	—	—	—	—	72 : 28
2	,,			62·15	26·47	5·29	5·00	—	—	1·08	0·63	trace	—	70 : 30
3	VII. Cent. (T'ang Dyn.); excav. in China			70·11	24·28	5·59	—	0·22	—	—	—	„	—	74 : 26
4	"			67·56	27·57	5·43	—	0·37	—	—	—	„	—	71 : 29
6	I. Cent. (Han Dyn.) ½ excav. in Japan		Fig. 1	62·99	24·12	3·97	—	—	2·63	—	1·83	—	—	72 : 28
7	"			67·22	25·44	0·61	6·73	—	—	—	—	—	—	72 : 28
8	"			65·82	28·72	5·05	—	—	—	—	—	—	—	70 : 30
9	"			68·63	30·69	0·69	—	—	—	—	—	—	—	69 : 31
10	*Japanese bronze mirror. V. Cent. (made in Japan); excav. in Japan.	Pale yellow		67·03	22·45	8·99	—	—	—	—	—	—	—	75 : 25
11	Corean bronze mirror. Not certain		Fig. 2	65·37	21·90	9·08	—	—	0·44	2·60	1·52	—	—	75 : 25
12	Corean bronze mirror. X. Cent.; excav. in Corea	Deep yellow	Fig. 2	72·99	11·76	15·14	—	0·29	—	•	—	0·09	0·23	—
13	Japanese bronze mirror. XI. Cent.; preserved in Japan	,,	Fig. 3	74·04	0·29	5·67	—	0·89	1·08	1·55	0·88	—	—	—
14	Chinese bronze mirror. XII. Cent. (Kin Dyn.); found in China	,,	Fig. 4	65·11	20·49	11·58	—	—	0·13	2·35	0·34	—	—	—
15	Chinese brass. XIX. Cent. (Ch'in-Dyn.); preserved in China		Fig. 5	74·00	3·29	7·59	12·96	trace	—	1·81	0·35	—	—	—
16	,,			58·52	5·58	7·66	23·29	1·78	—	—	3·17	—	—	—

* Recipe of a Japanese mirror at Yongishiki : 76 per cent. of copper to 24 per cent. of tin.

As may be seen from the table, the white bronze was made from the first century, and probably from much earlier times, down to the seventh century. It contains, on the average, 67 per cent. of copper, 27 per cent. of tin, and 6 per cent. of lead as its principal constituents, the average ratio of copper to tin being 71 : 29 ; the alloy corresponds, therefore, with the ε-phase in the copper-tin diagram, which is a solid solution of tin in copper, and known as specular metal. The presence of lead is not to be regarded as useless ; it reacts with neither copper nor tin, but lies between the granules of the solid solution, acting as a cement. The author was able to make a very good bronze mirror with these constituents. Without lead, the product is too brittle to be polished. Too slow cooling must, naturally, be avoided, in order to prevent separation of the lead. The ancients were clever enough to take advantage of the great hardness of the white bronze ; the figures on the back of such mirrors usually consist of very fine, but deeply cut, lines, which have resisted wear for two or three thousand years.

However bright the white bronze mirror may be, its reflective power is not so great as that of a silver mirror, absorption of the light taking place very much in the blue. A determination with the author's imitation metallic mirror gave the following figures : blue 40 per cent., yellow 50 per cent., and red 60 per cent. The objects reflected therefore seem much redder than they are in reality.

Weapons.

As weapons must be both hard and tough, the white bronze cannot be used for their manufacture, and that the bronze with 10—20 per cent. of tin suits best seems a fact well known to the ancients. They knew, too, that in order to make the casting easier, some antimony could be added without any of the hardness being lost.

Two samples of arrow-heads of the Han dynasty were analysed with the following results :

	I.	II.
Copper	74·47	73·12
Tin	10·82	16·15
Antimony	8·00	8·69
Nickel	3·68	2·04
Iron	3·03	trace
Arsenic	trace	trace

Since antimony dissolves in copper as well as in tin, the above samples might be thought to be similar to one composed of 85 per cent. of copper and 15 per cent. of tin, ignoring the other small admixtures, but the alloys with the above compositions have

quite different structures, as is seen from those of the arrow-heads
shown in Figs. 6 and 7. An ingot with the same composition as
the arrow-head, No. 1, was prepared and quenched at 680° after
half an hour's heating. Its structure was changed from the
ordinary polygonal (Fig. 8) to the fine acicular (Fig. 9), which is
quite similar to that of the arrow-head. The hardness of the
bronze with 10 per cent. of tin is only 12 on Shore's scale, whilst
that of the arrow-head, No. 1, is 15—17. The author's imitation
sample was also 10—12 before quenching, but after quenching it
had risen to 15. The ancients had probably no intention of
quenching; they arrived at such a result unexpectedly by way of
moulding.

A Japanese arrow-head excavated in the Province of Tango has
the composition (I), and must certainly have been less sharp than

		I.	II.
Copper	....	96·48	90·28
Tin	....	2·46	3·20
Lead	....	0·56	0·28
Arsenic	....	0·50	0·03
Iron	....	—	5·60

those described above. The age is not certain, but a bronze coin,
"Wadô Kaihô," made in the seventh century, has almost the same
composition (II). They might perhaps have some relation to each
other.

Swords and halberds excavated in Japan and China were
analysed, with the following results:

Samples.	Copper.	Tin.	Antimony.	Arsenic.	Nickel.	Iron.	Lead.	Copper : Tin.	
Sword: Shantung, China.	73·34	19·84	3·80	0·55	2·47	—	—	78 :	22
Sword: Shantung, China.	69·31	12·55	2·30	3·01	3·52	1·37	7·92	84 :	16
Halberd: Shantung, China.	73·35	17·48	—	trace	—	—	9·17	80 :	20
Sword: Prov. of Chikuzen, Japan.	76·60	14·13	4·93	trace	2·93	0·09	1·32	84 :	16

The proportions of copper to tin are correct, but the large
amount of lead in some of them cannot be commended.

Musical Instruments.

Bell metal with a high percentage of tin is sonorous, but too
brittle. The ancients were in the habit of using an alloy with
rather less tin. An excavated Japanese bell, which dates from
about the eighth century A.D., has the composition (I):

	I.	II.
Copper	68·96	82·90
Tin	15·45	9·93
Lead	5·63	—
Antimony	8·32	2·60
Iron	0·04	1·38
Nickel	1·35	0·79
Arsenic	trace.	1·68
Gold	—	0·71

Statues.

A small gilded Buddhist statue of the Six Dynasties (third century) has the composition (II).

Money.

The ancient Chinese coins generally contain less tin with much lead, so that some of them can scarcely be called bronze. The following are the results of analyses made with a few kinds of Chinese money current at the time of the " Spring and Autumn Annals," 722—481 B.C. :

Coin.	Copper.	Tin.	Lead.	Antimony.	Iron.	Arsenic.	Nickel.	Silver.
Bell money...	67·53	16·52	10·84	1·83	—	2·36	0·92	—
Knife money	46·22	9·25	43·53	—	0·73	—	—	0·27
,, ,,	38·38	1·66	55·41	—	2·66	0·60	1·03	—
,, ,,	45·93	2·12	48·60	—	—	1·72	1·63	—
,, ,,	42·25	2·12	47·32	—	—	3·28	5·08	—
,, ,,	64·65	6·76	21·25	—	0·41	3·88	3·04	—
Spade money	70·42	9·92	19·30	—	—	—	0·35	—

Spoons, etc.

Corean bronze, called "Sahari," or sometimes "Sonorous copper," usually occurs in the form of spoons, water-pots, etc. Very old spoons are usually covered with a velvet-black rust, but seldom with green carbonates. They give, on analysis, the following numbers :

	Copper.	Tin.	Nickel.	Zinc.	Arsenic.	Iron.	Lead.
Ancient spoon	73·77	24·04	2·19	—	—	—	—
New ,, ...	77·19	21·62	—	0·20	—	—	—
Ancient water pot ...	77·89	19·35	—	—	3·82	0·09	0·77

The alloy is therefore similar to the pale yellow bronze mirror. It sometimes exhibits a very beautiful structure consisting of large crystals. α and ε. The alloy is strongly resistant against rusting and is well suited for the purpose to which it is put by the Coreans.

Helium : its Production and Uses.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON JUNE 17TH, 1920.

By JOHN CUNNINGHAM McLENNAN.

ɪɴ 1868 Janssen (*Compt. rend.*, 1868, **67**, 838) drew attention to he existence of certain lines hitherto unobserved in the solar pectrum, which we now know are given by the element helium. ɪn the same year, Frankland and Lockyer (*Proc. Roy. Soc.*, 1868, [7, 91), from their observations on these spectral lines, were led o announce the existence of an element in the sun which up to hat time had not been found on the earth. To this element they ɡave the name helium.

In 1882 the discovery was made by Palmieri (*Gazzetta*, 1882, **12**, 556) that the helium spectrum could be obtained from rocks and lavas taken from Vesuvius.

In the United States of America, Hillebrand in 1890 (*Bull. U.S. Geol. Survey*, 1890, No. 78, p. 43) succeeded in obtaining a quantity of gas from the mineral uraninite, which from chemical ʌnd spectroscopic tests he concluded was nitrogen. This gas we ɴow know was, in fact, helium.

Finally, in 1895, Sir William Ramsay (*Chem. News*, 1895, **71**, 151) discovered that a gas could be obtained from the mineral cleveite. This gas he purified, and, on examining its spectrum, he found it to be the long-sought for element helium. From 1895 up to the present, investigation has shown that helium is widely diffused throughout the earth. It can be obtained from many types of rocks, minerals, and earths, and it is present in varying amounts in practically all natural gases and spring waters. It is present too in the atmosphere of the earth to the extent of about four parts in one million by volume.

The gases from some springs in France have been shown to contain as much as 5 per cent. of helium. In the Western States of America, especially in Texas, natural gases exist which contain from ı to 2 per cent. of helium, but within the British Empire no natural gases which have been examined show a helium content as high as 0·5 per cent.

Until the spring of 1918, not more than 3 or 4 cubic metres of um had, in the aggregate, been collected, and its market price, ugh variable, was about £300 per cubic foot.

The principal characteristics of helium are :

1) Its extreme lightness. It is only twice as heavy as hydrogen, the lightest element as yet isolated.

M M*

(2) Its absolute inertness. All attempts to effect combinations of helium and the rare gases, neon, argon, krypton, and xenon, as well, with other elements have as yet failed.

(3) Its close approximation to an ideal or perfect gas. It is monatomic, and is liquefiable at a temperature below that of liquid hydrogen. By causing liquid helium to evaporate in a vacuum, Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 493) has succeeded in reaching a temperature within 1° or 2° of the absolute zero.

(4) Its low sparking potential. Electric discharges can be passed through helium more easily than through most other gases.

No element has had a more romantic history than helium, and none is of greater interest to men of science than is this gas at the present time. Its formation as a disintegration product of the radioactive elements, and the identity of the nuclei of helium atoms with α-rays, give it a unique position among the elements.

Intense interest has been aroused by Sir Ernest Rutherford's recent discovery that in the nuclei of helium atoms in the form of α-rays we have a powerful and effective agent for disintegrating and simplifying the nuclei of atoms generally. This discovery points the way to still further progress. In the past, helium has been considered a rare and precious gas. To-day it is being produced in large quantities, and in view of the proposal now being put forward to use this gas in place of hydrogen as a filling for airships, one is apt to consider it to be not so precious as heretofore. It may be, however, that such vast and vitally important directions will suddenly be opened up in which helium can be utilised that the conservation of the gas, while it is still available to us, will become a matter of the first importance.

Shortly after the commencement of the war in 1914, it became evident that if helium were available in sufficient quantities to replace hydrogen in naval and military airships, losses in life and equipment would be very greatly lessened.

The fact that helium is both non-inflammable, non-explosive, and possesses 92 per cent. of the lifting power of hydrogen, makes it a most suitable filling for airship envelopes. By the use of helium, the engines of airships can be placed within the envelope if desired. A further advantage possessed by helium over hydrogen is that the buoyancy may be increased or decreased at will by heating and cooling the gas by electric or other means, which fact may possibly lead to considerable modifications in the technique of airship manœuvring and navigation. Moreover, the loss of gas from diffusion through the envelope is less with helium than with hydrogen to the extent of about 30 per cent.

Although there are indications that proposals had been put forward during the war by men of science in allied and enemy countries, as well as in the British Empire, regarding the development of supplies of helium for aeronautical purposes, it should be stated that the movement that led up to the investigation which it was my privilege to undertake was initiated by Sir Richard Threlfall. The existence in America of supplies of natural gas containing helium in varying amounts was known to him and others, and preliminary calculations as to the cost of production, transportation, etc., which he made led him to believe that there was substantial ground for thinking that helium could be obtained in large quantities at a cost which would not be prohibitive.

His proposals were laid before the Board of Invention and Research of the British Admiralty, and in the autumn of 1915 the author was asked by that Board to determine the helium content of the supplies of natural gas in Canada, and later on of those within the Empire, to carry out a series of experiments on a semi-commercial scale with the helium supplies which were available, and also to work out all technical details in connexion with the production of helium in quantity, as well as those relating to the re-purification, on a large scale, of such supplies as might be delivered and become contaminated with air in service.   The present paper aims at giving a brief account of this investigation.

Composition of the Natural Gases Investigated.

In commencing the investigation, a survey was made of all the natural gases available in larger or smaller quantities within the Empire with a view to ascertain their helium content. Natural gases from Ontario and Alberta, Canada, were found to be the richest in helium, and these sources, it was found, could supply m 10,000,000 to 12,000,000 cubic feet of helium per year. The lowing is a summary of the results obtained from the analyses a number of the gases investigated. They include, it will be en, a few samples from outside the Empire. For a complete count of this part of the investigation, the reader is referred to alletin No. 31 of the Mines Branch. Department of Mines. anada. 1920.

(a) *Ontario Gases.*—The analysis made by Profs. Ellis, Bain, and Ardagh *(Report of Bureau of Mines of Ontario*, 1914) of the ttural gases supplied to the experimental station, initially set at Hamilton, Ontario (Blackheath System), is as follows:

Methane	80 per cent.	
Ethane	12	,,
Nitrogen	8	,,

M M* 2

It was found, however, on operating with this gas that the percentage assigned to methane really included a considerable proportion of gasoline, pentane, and butane as well. The helium content of the gas was found to be 0·34 per cent.

(b) *Alberta Gases.*—Gas taken from the mains leading from the Bow Island supply to Calgary was found to be quite free from the heavier hydrocarbons. At times it contained slight amounts of water vapour and occasionally a trace of carbon dioxide as well. Its approximate composition is given under I.

	I.		II.	
Helium	0·33 per cent.		0·36 per cent.	
Methane	87·6	,,	91·6	,,
Ethane	0·9	,,	1·9	,,
Nitrogen	11·2	,	6·14	,,
Carbon dioxide	trace		trace	
Water vapour	trace		trace	

One well in particular, namely, No. 25 Barnwell, which has recently been driven, and now supplies gas to the system, was found to have a product of the composition II.

(c) *New Brunswick Gases.*—Some natural gases obtained from wells struck near Moncton, New Brunswick, Canada, were examined, and found to have the following composition:

Methane	80·0	per cent.
Ethane	7·2	,,
Carbon dioxide	None	
Oxygen	None	
Nitrogen	12·8	per cent.
Helium	0·004	,,

(d) *New Zealand Gases.*—A series of samples of the natural gases from the Hanmer, Kotuka, Weber, Blairlogie, and Rotoru: supplies in New Zealand were forwarded by Mr. J. S. McLaurin Dominion Analyst of Wellington, New Zealand, for examination but were found to have an insignificant helium content, the riches: containing not more than 0·077 per cent.

(e) *Italian Gases, Pisa.*—A sample of the natural gas brought by pipe to the city of Pisa, in Italy, was examined, and found to have the following composition:

Methane	80·0 per cent.
Ethane	4·0	,,
Carbon dioxide	3·5	,,
Nitrogen	11·9	,,
Oxygen	0·6	,,
Helium	None	

(f) *Miscellaneous Analyses.*—An analysis of the natural gas supply from Heathfield, Sussex, England, showed it to have a helium content of but 0·21 per cent. The gas from the King

Spring, Bath, England, was found to contain 0·16 per cent. of helium, and analyses of natural gases obtained from Trinidad and from Peru showed their helium content to be negligible.   An interesting observation was made in connexion with natural gases obtained from Pitt Meadows, Fraser River Valley, and Pender Island, in the Gulf of Georgia, British Columbia.   Both these gases were found to have a nitrogen content of more than 99 per cent.

Preliminary Experiments.

Soon after taking up the investigation, it was found, as mentioned above, that large supplies of helium were available in the natural gas fields of Southern Alberta, and that a small supply could be obtained from a gas field situated about twenty-five miles to the south-west of the city of Hamilton, in Ontario.   In 1917 the Board of Invention and Research decided to endeavour to exploit these sources of supply, and operations were begun by setting up, as already stated, a small experimental station near the city of Hamilton.

At this station, efforts were directed towards constructing a machine which would efficiently and economically separate out the helium from the other constituents present in the natural gas. The carrying out of this work expeditiously was made possible through the hearty co-operation of L'Air Liquide Société of Paris and Toronto, who generously lent, free of cost, a Claude oxygen column and the necessary auxiliary liquefying equipment for the investigation.

By making suitable additions to, and modifications in, this oxygen rectifying column, it was ascertained that the problem of separating, on a commercial scale, the helium which was present in this crude gas to the extent of only 0·33 per cent. was one capable of satisfactory solution.   Early in 1918 it was found possible to raise the percentage of helium in the gas to 5·0 by passing it through the special rectifying column once only, and as the gas obtained in this way consisted of nitrogen and helium with a small percentage of methane, it became therefore a comparatively simple matter to obtain helium of a high degree of purity.   In one particular set of experiments on this final rectification, helium of 7 per cent. purity was obtained.

Experimental Station at Calgary, Alberta.

In order to operate on the natural gas of the Bow Island system of Southern Alberta, an experimental station was established at Calgary in the autumn of 1918, and, starting with the knowledge

acquired through the preliminary operations at Hamilton, rapid progress was made in developing a rectification and purifying column, together with the requisite auxiliary equipment, which would efficiently and cheaply separate the helium from the natural gas.

The experimental station at Calgary consisted of a brick building of moderate dimensions, a small brick hut, and a galvanised iron balloon shed, located on the property of the Canadian Western Natural Gas, Light. Heat, and Power Company. The equipment in these buildings included that necessary to furnish an adequate supply of gas, which consisted of the requisite piping, gate valves, pressure-reducing valves, etc., a gasometer and two balloons, a number of gas cylinders, and the rectifying column with its expansion engine, together with the necessary compressors and a complete gas-testing outfit.

Development of the Rectification Column.

In proceeding to develop an equipment for separating the helium from the other constituents of natural gas, three lines of attack appeared to be open, namely, (a) by producing the refrigeration necessary to liquefy all the gases except the helium by the cold obtainable from the natural gas itself, (b) by using external refrigeration entirely, such as that obtainable with ammonia, carbon dioxide, liquid air, liquid nitrogen, etc., and (c) by combining methods (a) and (b).

The last method had been successfully used for the production of helium by the naval authorities of the United States in the Texas field, but from the information supplied it did not appear that this process could be considered to be an economical one.

The preliminary experiments at Hamilton, Ontario, made it abundantly clear that method (a) was very promising and likely to be both efficient and economical. It was therefore adopted. It was evident from the start that to produce an efficient method the main difficulty to overcome would be the securing of a proper balance between the heat exchangers, the liquefier, the vaporisers, and the rectification portions of the machine. A machine was therefore designed, constructed, and supplied with piping which possessed great flexibility, and, in its general scheme, followed the lines of the Claude oxygen-producing column. It is unnecessary to go into details regarding the operation of this machine. It will suffice to say that it was tested under a variety of conditions. Notes were taken of the temperatures reached at different points in the machine under equilibrium conditions when the gas was passed through it in various ways. As a result of this procedure,

4th Vap. 5th Vap.   15.   He. outlet

12a

35a

12a   5a

10A

8.

To balloon.

35e

K

13.

14.

4th Exchanger. 3rd Exchanger.

P.B comp.

35a

Vap.

P1

6

P2   7

2

9   11

† Indicates location of Thermo couple.

→ Indicates gas containing He.

⇾ Indicates liquid.

>— Indicates exhaust gas.

E

10   1   1   0   (16)   (16)   V   1   SC

Pot. First Vap   Sec Vap
(4)   (7)   (2)   (5)   (16)   (16)   (15)   (12)   (3)

it was soon found what parts of the machine could be eliminated
and what parts could be modified with advantage. When those
changes were made which seemed desirable in the light of the
experience gained, it was found that a machine had been evolved
which would give highly satisfactory results.

A sketch of the experimental machine as it was finally con-
structed is shown in Plate I. With this machine, the process of
separating the helium consisted of two operations. In the first, the
compressed gas was passed through the heat exchangers, thence
through the liquefier and the expansion engine to the bottom of
the column at A. The uncondensed gas passed up through the
first vaporiser, then through the valve, No. 12, to B. What was
still uncondensed passed out through valve No. 18 to the bottom of
the rectification column H and up over the third vaporiser, where
more of the gas was condensed, and the final product, containing
from 5 to 6 per cent. of helium, was drawn off. The liquid from
A was passed through the valve C to the fourth vaporiser, from
which it would overflow into the second vaporiser. The condensed
liquid from B could be passed through D to the fourth vaporiser
or through valve No. 7 to the third vaporiser. Some of the cool-
ing liquid in the second vaporiser could also be passed through
valve No. 6 to the third vaporiser when desired. In the second
operation, the first product, containing 5 per cent. of helium, the
remainder being principally nitrogen with a small percentage of
methane, was compressed by a small compression pump to from
20 to 30 atmospheres, and passed through the third and fourth
heat exchangers to the fourth vaporiser. Here some of it was
condensed by the liquid methane produced in the first operation,
and this condensed liquid flowed into the collecting bottle, K.
The uncondensed gas still at 20 to 30 atmospheres passed, as shown
in the sketch, into the fifth vaporiser, where almost all the nitrogen
was condensed, and the final product was drawn through valve
No. 15. The fifth vaporiser, it will be seen, was supplied with
the liquid drawn from the bottle, K. It could also be supplied,
if desired, by liquid from the fourth vaporiser through the valve
No. 10. The level of the bottle was so arranged that there would
be about 3 or 4 inches of liquid at the bottom before it showed
on the gauge. By keeping the liquid just showing in the gauge,
it was possible to prevent the gas from being drawn off with the
liquid. In order to keep the temperature in the fifth vaporiser
as low as possible, the gas from the evaporating liquid in it was
drawn off through the third and fourth heat exchangers by means
of a powerful vacuum pump.

In operating with this machine, it was found that helium of

87 to 90 per cent. purity could be regularly and continuously produced.

Operations.

The experimental machine just described was used continuously for a series of trial runs from December 1st, 1919, to April 17th, 1920. The object of carrying out these trials was to gain as much knowledge as possible of the best running conditions. In the

FIG. 1.
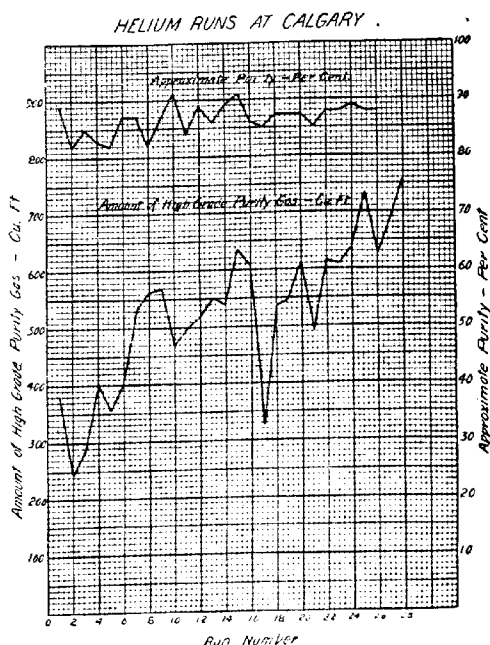
course of the four months' operations, numerous small modifications were made in the apparatus. Losses due to leaks were stopped and valve regulation was greatly improved. As a result of the operations, a steady increase was made in the output of helium of high purity.

The trials were made in successive runs, as it was necessary to shut down at intervals to refill the desiccators with sodium hydroxide.

In making a run, about 500,000 cubic feet were passed through the machine, and from this amount upwards of 20,000 cubic feet of the gas, containing 5 to 6 per cent. of helium, was obtained. As this low-grade product was made it was stored in a large balloon, and the residual gas was passed back into the mains for use in the city of Calgary. The 5 to 6 per cent. product was compressed to from 20 to 30 atmospheres, and then passed through the fourth and fifth vaporisers, as described above. The amount of final product, of 87 to 90 per cent. purity, obtained in each run rose steadily in the course of the operations from about 300 cubic feet to more than 700 cubic feet per run. From this it will be seen that the efficiency obtained with each of the two operations was about 67 per cent. In special runs made under exceptionally good conditions, a still higher efficiency was obtained. One of the curves given in Fig. 1 shows that the purity of the high-grade final product was steadily maintained in the series of runs, and the other curve exhibits the steady increase made in the production of helium of high-grade purity.

High-grade Purification.

When it was seen that the highest purity obtainable with the experimental machine under actual running conditions was about 90 per cent., steps were taken to design and construct an auxiliary piece of apparatus for raising the purity of the gas up to 99 per cent. or higher. This apparatus is shown in Plate II. *A* and *F* were two receptacles which could be kept partly filled with liquid air or liquid nitrogen. In operating this piece of apparatus, a high vacuum was maintained in *A*, but the liquid in *F* was allowed to evaporate at atmospheric pressure. It was arranged that the gases from both receptacles could be conserved by collecting them in a gasometer, and so rendering them available for use over and over again in closed cycle by the auxiliary liquid air or liquid nitrogen machine. In order to obtain a product of very high purity with this apparatus, the gas containing 87 to 90 per cent. of helium was compressed to 100 atmospheres. It entered the apparatus at *G*, passed through the heat-exchanging coils in *B*, thence through a second heat exchanger in *C*, where it was cooled still further by the vapour from the liquid in *C*. From this it passed through a coil immersed in the liquefied gas in *F*, and thence into the rectification column, *D*. Thence it passed up through a set of tubes in *A*, where its temperature could be lowered to approximately – 200° by the surrounding liquid and vapour. As shown in the diagram, the purified gas passed out through a high-pressure valve, *E*, and thence through the exchanger, *B*, to

PLATE II.
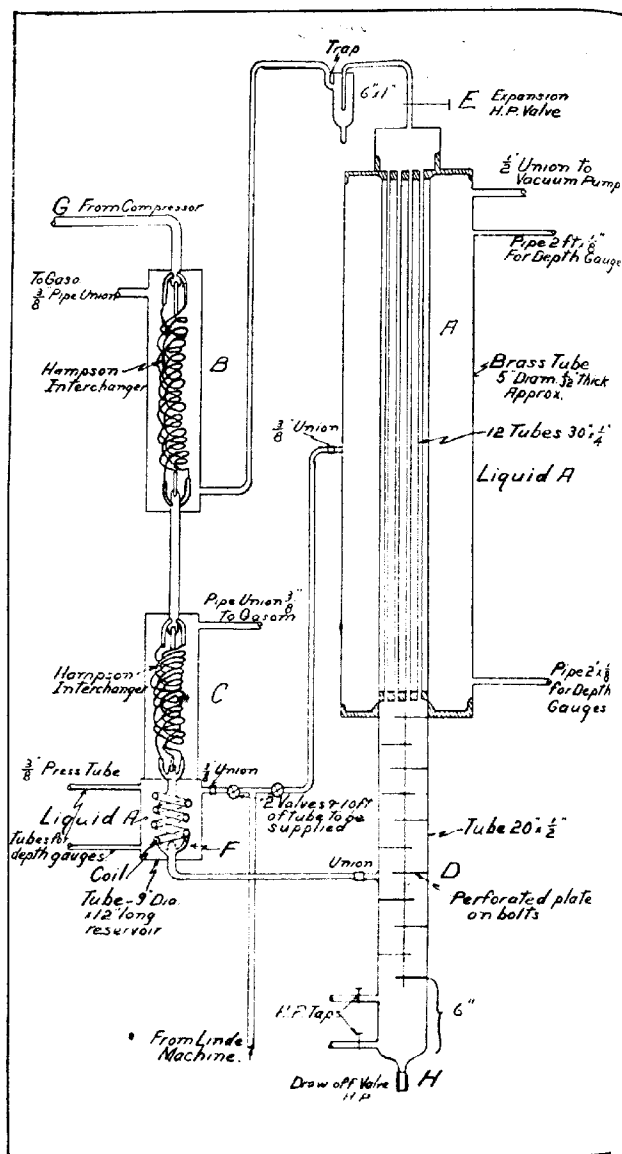
a gasometer, where it could be stored prior to being compressed into cylinders. All gases which were condensed in the tubes in A or in the column D could be run off at H. As the pressure of nitrogen is less than half an atmosphere at -200°, it was estimated that, by maintaining the gas containing 87—90 per cent. of helium at 100 atmospheres in the whole apparatus, the final product must necessarily have a purity of more than 99 per cent. As the apparatus was designed, it will be seen that it could be used, not only for obtaining a product of high purity at the works, but also for purifying helium which became contaminated with air by use in balloons in service. Through numerous delays experienced in obtaining delivery of tubing, liquefying equipment, etc., this purifying apparatus has not been given any more than a preliminary trial. From this, however, it is quite evident that it will prove satisfactory in operation. For the purpose of carrying out this scheme of high-grade purification, a liquid-air plant was installed by the University of Toronto. Motors and an electric current supply were furnished by the Hydro Electric Commission of Ontario, and a special financial grant was made by the Honorary Advisory Council for Scientific and Industrial Research of Canada to supplement that made by the Admiralty and the Air Board of Great Britain.

Final Design of Helium-extracting Apparatus.

From the foregoing it will be seen that every step in the production of high-grade helium has been carefully examined and tested. From the experience gained, we have been able to draw up specifications for a commercial plant which will enable one to meet the whole of the natural gas of the Bow Island supply in Alberta. The unit proposed will deal with about 1600 cubic metres or 56,500 cubic feet of gas per hour at normal pressure and temperature. At the altitude of Calgary, this would be equivalent to 82,200 cubic feet per hour. The machine would easily cope with 66,000 cubic feet per hour or 1100 cubic feet per minute. Of these machines, six would deal with 9,500,000 cubic feet of gas a day, and would thus take about the average daily supply available from the field, as based on records of the average yearly consumption. In order to have sufficient machines to operate regularly to capacity, it would probably be advisable to have eight helium columns included in the plant.

The cost of a commercial plant suitable for treating the whole of the supply of the Alberta field would probably be less than £150,000). The amount of helium of upwards of 97 per cent. purity obtainable per year from the field would be about 10,500,000

cubic feet. This is based on the assumption of an efficiency of 80 per cent., which experience has shown is obtainable. As to operating costs, our experience has shown that, allowing for interest on the investment, a ten years' amortisation, salaries, supplies, and running charges, helium can be produced at the Alberta field for considerably less than £10 per 1000 cubic feet. This sum does not, of course, include the cost of purchasing cylinders or of transporting them from and to the works. Neither does it include any compensation to the owners of the field for the supply of gas. The column as finally designed for the production of helium of approximately 97 per cent. purity is shown in Plate III. It is not drawn to scale, but it conforms on general lines to the standard oxygenen-nitrogen machines of L'Air Liquide Société. It consists of :

I. Two exchangers of temperature. one of which, Q, is shown, the two being so arranged that the flow of gas through them can be reversed. as is the present practice in the oxygen and nitrogen machines. The high-pressure gas is in the outer casing, and the return low-pressure gas in the small tubes; the heads are provided with three sections, so that the low temperature of the outgoing gases can be utilised.

II. A liquefier, R. This is the same as the liquefier in the standard machines, but it has only one of the returning gases flowing through it.

III. An expansion engine, S. This engine is of the standard type used in the oxygen and nitrogen machines.

IV. A first vaporiser and pot, U, T. This vaporiser. with pot for collecting liquid. is the same as on the standard nitrogen column.

V. A second vaporiser and pot, W, V. This vaporiser, with the pot, is similar to the second vaporiser now used on the standard nitrogen columns. It should be about one-third the size of the first vaporiser, U.

VI. A rectification column, X. This column should stand a pressure of 10 atmospheres and have a collecting basin at the bottom. Its diameter should be about three-eights of that of the vaporisers U or W. Its length should not exceed 2 feet.

VII. A vaporiser, Y. The diameter of this vaporiser is the same as that of the rectification column, X. and its length should not exceed 2 feet. On this vaporiser. a partial vacuum is maintained.

VIII. Two collecting bottles, Z_1, Z_2.

IX. Two exchangers of temperatures. one of which, I, is shown. These are similar to Q, and should be reversible, but their capacity is only 6 per cent. of Q.

X. A vaporiser, *II*. This vaporiser should be of the same size as *Y*, and the high-pressure side of it should stand a pressure of 50 atmospheres.

XI. A rectification column, *III*. This column should stand a pressure of 50 atmospheres, and should be about half the diameter of the column *X* and about 3 feet long.

XII. A vaporiser, *IV*. This should be similar to vaporiser *II*, but only half the diameter; on this vaporiser a partial vacuum is maintained.

XIII. The control valves are designated by letters from *A* to *N*, fourteen in all.

XIV. The outlets are designated by P_1, P_2, etc., eleven in all.

XV. The gauges are designated by the numbers in parenthesis, thus, (1), (2), etc., eleven in all.

XVI. The levels for showing the depth of liquid are designated by L_1, L_2, etc., seven in all.

XVII. The method of connecting up is shown in the figure.

The method of using the column is as follows.

The First Process.—(*a*) The compressed gas enters the exchangers, *Q*, through valve *A*, and, after passing out of the exchanger at the top, some of it goes through the liquefier, *R*, and the rest of it through the expansion engine, *S*, to the first pot, *T*. In *T* the pressure is about 4 atmospheres, and most of the gas is liquefied in the condenser, *U*. The uncondensed part passes through the valve *H* into *V*, where more of it is liquefied in the condenser, *W*. The still uncondensed gas flows through valve *I* to the bottom of the rectification column, *X*; it passes up through the column, through the condenser *Y*, where more of it is liquefied, and the rest, which now contains about 5 per cent. of helium, passes through valve *K*, where the pressure is reduced to nearly atmospheric, and it passes through the inner section of the exchanger to a gasometer.

(*b*) The liquid that collects in the pots *T* and *V* is drained into the bottles Z_1 and Z_2, which are made fairly long, and the bottom ends of the levels are about 6 inches from the bottom, so that it is possible always to keep liquid in the bottom of the bottles and prevent any uncondensed gas escaping. The liquids from the bottles Z_1 and Z_2 are passed through the valves *D* and *E*, respectively, into the vaporiser, *II*; in addition, the liquid from Z_2 can also be run into the vaporiser, *Y*, through valve *F*. The liquid in the vaporiser *II* overflows into the vaporiser *II'*, and it overflows from *II'* into the first vaporiser, *U*. Some of the liquid in the vaporiser *II* can be passed through the valve into *Y*. Liquid that condenses in *Y* flows down through the rectification

trays in _X_, and is passed through the valve _J_ into the vaporiser _W_.

(c) The gases from the evaporating liquids in the vaporisers _U_ and _W_ pass directly back to the liquefier, _R_, and from the liquefier to the exchanger, _Q_, as shown in the diagram. The gas evaporated in vaporiser _II_ flows with the liquid down into vaporiser _W_. The gas evaporating under vacuum in vaporiser _Y_ passes out through the exchanger, _Q_, to the vacuum pump.

The Second Process.—(_d_) The gas containing helium drawn off in the first process through the valve _K_ is re-compressed to 30 atmospheres, and passes through the exchanger _I_ to the top of the condenser _II_; it flows down through _II_, where part of it is liquefied, and the liquid and gas pass into the rectification trays, _III_, to the collector at the bottom, the gas passing up through the column to the condenser _IV_, where the rest of the nitrogen is condensed, and the product, containing about 97 per cent. of helium, is drawn off through the valve _M_.

Notes on Special Points.

The vaporiser _Y_ is the coldest part of the machine in the first process, owing to the liquid boiling under a partial vacuum. The liquid produced in the condenser runs down through the rectification trays in _X_, and the uncondensed gas from _W_ passes up through it. Any helium and most of the nitrogen in the liquid will be recovered, and a large part of the methane in the gas will be condensed. Thus the product drawn off through _K_ will contain very little methane.

In the second process, the gas containing 5 per cent. of helium under about 30 atmospheres pressure flows from the top to the bottom of the vaporiser _II_. This vaporiser is filled with the liquid produced in the first process, and is at the temperature of liquid methane (–163°). At this temperature, nitrogen condenses at about 12 atmospheres, and much of it is condensed. The liquid and gas both flow over a few trays, and the helium dissolved in the liquid would be recovered. The uncondensed gas flows up through the trays, and is cooled and partly condensed by the cold liquid from _IV_. The liquid is gradually warmed, and thus any helium in it will be recovered.

Miscellaneous Investigations.

In the course of the investigation on the development of a machine for extracting helium from natural gas, supplies of helium of varying degrees of purity became available. These were highly purified, and were used for the investigation of certain collateral

problems which demanded solution. Among the results obtained, it was found that for aeronautical purposes hydrogen could be mixed with helium to the extent of 15 per cent. without the mixture becoming inflammable or explosive in air. Mixtures containing even as much as 20 per cent. of hydrogen could be burnt or exploded only when treated in an exceptional manner. The permeability of rubbered balloon fabrics for helium was shown to be about 0·71 of its value for hydrogen. For skin-lined fabrics, the permeability to hydrogen and helium was about the same. Thin soap films were found to be about one hundred times more permeable to hydrogen and helium than rubbered balloon fabrics, but untreated cotton fabrics when wetted with distilled water were but feebly permeable to these gases. It was found that rapid estimations of the amount of helium in a gas mixture could be made with a pivoted silica balance, a Shakspear katharometer, or a Jamin interferometer.

The latent heats of methane and ethane have been determined, as has also the composition of the vapour and liquid phases of the system methane–nitrogen. It has also been shown that helium containing as much as 20 per cent. of air, oxygen, or nitrogen can be highly purified in large quantities by simply passing it at slightly above atmospheric pressure through a few tubes of cocoa-nut charcoal kept at the temperature of liquid air. In the spectroscopy of the ultraviolet, helium has been found to be exceptionally useful. Arcs in helium between tungsten terminals can be easily established and maintained. In a particular investigation with a vacuum grating spectrograph, it was found that by the use of arcs in helium under 30 cm. pressure, illumination could be maintained continuously for hours, and with such arcs spectra could easily be obtained extending to below 1000 Å.U.

Although it is known that free electrons can exist in highly rarified helium to an amount easily measurable. it was found that pure helium under a pressure of more than 80 atmospheres did not exhibit anything in the nature of metallic conduction. Moreover, the mobilities of both positive and negative ions formed by rays in helium under this high pressure were found to have about one-third the value expected on the basis of an inverse pressure law.[*]

[*] The following is a list of the papers which deal with the subjects mentioned : (1) " Report on some sources of Helium in the British Empire " (McLennan, *Bulletin No.* 31. *Mines Branch, Department of Mines, Canada,* 1920. (2) " The Estimation of the Helium Content of Gases by the use of a katharometer " (Murray, *Trans. Roy. Soc., Canada,* 1919. 27). (3) " The use of the Jamin Interferometer for the Estimation of small amounts of

The Uses of Helium.

The investigation into the problem of producing helium in large quantities was originally undertaken with a view to the utilisation of the gas in aeronautical warfare. The investigation has shown that it can be produced at a cost which is not excessive, but 'it has also been shown that from the sources in the Empire which are known and have been examined, the supply of helium cannot be greater than about 12,000,000 cubic feet per year. This quantity clearly would be sufficient to keep only a very few of our airships of the larger type in commission, even if the gas were diluted to the extent of 15 per cent. with hydrogen. This amount would, however, suffice to keep a number of the smaller aircraft supplied. Moreover, it might be used to fill fireproof compartments adjacent to the engines if it were ever decided to instal these within the envelopes of our larger airships.

Since it has been demonstrated that helium can be produced in quantity, one is led naturally to consider in what directions one can hope to use the gas other than that originally intended. In industry it may be used as a filling for thermionic amplifying valves of the ionisation type. It may also be used for filling tungsten incandescent filament lamps, especially for signalling purposes where rapid dimming is an essential, and for producing gas arc lamps in which tungsten terminals are used, as in the "Pointolite" type. Both of these varieties of lamps possess the defect, however, of soon becoming dull owing to the ease with which incandescent tungsten volatilises in helium, and deposits on the surface of the enclosing glass bulbs. As regards illumination, helium arc lamps possess an advantage over mercury arc lamps in that the radiation emitted has strong intensities in the red and yellow portion of the spectrum.

Helium or Hydrogen in Air " (McLennan and Elworthy, *ibid.*, p. 19). 4) "The Permeability of Balloon Fabrics to Hydrogen and Helium" (Elworthy and Murray, *ibid.*, p. 37). (5) " Composition of the Vapour and Liquid Phases of the System Methane–Nitrogen " (McTaggart and Edwards, *ibid.*, p. 57). (6) "A Continuous Flow Apparatus for the Purification of Impure Helium Mixtures " (Edwards and Elworthy, *ibid.*, p. 47). (7) " On the Combustibility of Mixtures of Hydrogen and Helium " (Satterly and Burton *ibid.*, p. 211). (8) " On the Latent Heats of Methane and Ethane " (Satterly and Patterson, *ibid.*, p. 123). (9) " On the Mobilities of Ions in Helium at High Pressures " (McLennan and Evans, *ibid.*, 1920). (10) " On the Permeability of Thin Fabrics and Films to Hydrogen and Helium " (McLennan and Shaver, *ibid.*). (11) " Spark Spectra of Various Elements in Helium in the extreme Ultra-violet " (McLennan and Lewis, *ibid.*). (12) " Arc Spectra in vacuo and Spark Spectra in Helium of Various Elements " (McLenran, Young, and Ireton, *ibid.*).

It has been shown by Nutting (*Electrician*, March, 1912) that Geissler tubes filled with helium are eminently suitable, under certain conditions, for light standards in spectrophotometry, but the amount of the gas which could be used in this way is very small.

In spectroscopy, especially for investigations in the ultra-violet region, helium is invaluable. Doubtless its use in this field will be rapidly extended. The use of the gas in physical laboratories generally, and especially where certain investigations on the properties of matter are carried out, will also be greatly increased.

It has recently been proposed to use helium in place of oil for surrounding the switches and circuit-breakers of high-tension electric transmission lines. If the gas should prove suitable for this purpose. large quantities could be utilised. but it has yet to be demonstrated (and it is not clear that it can be) that in this field helium possesses any advantage over the oils now used.

It has been suggested by Elihu Thomson and others that if divers were supplied with a mixture of oxygen and helium, the rate of expulsion of carbon dioxide from the lungs might be increased. and the period of submergence as a consequence be considerably lengthened.

It is probable, however, that in the field of low temperature research helium will immediately find its widest application. For this work, helium is unique in that. when liquefied and possibly lidified, it enables one to reach the lowest temperatures attainible. Every effort should be directed towards the exploitation of ; use in this direction.

One point that is important and should not be overlooked is that e supplies of natural gas from which helium can be extracted ? being rapidly used up. When our natural gas fields are :leted, it would appear that our main source of supply of helium ?ll have disappeared. Careful consideration should, therefore, be ren to the problem of producing helium in large quantities while ?s still available. and of storing it up for future use. As already ated. it may be that in the future it will be of paramount ?portance to have even a moderate supply of the gas available.

A Cryogenic Laboratory.

To chemists and physicists especially, the discovery that helium ?n be produced in quantity at a moderate cost opens up a vista ! the realm of low temperature research of surpassing interest. ? means of liquid oxygen, the properties of substances can be ?died down to a temperature of --182·5°. Liquid nitrogen pro-?es us with a temperature of --193·5°, and hydrogen, which was

originally liquefied in 1898 by Sir James Dewar, enables us to reach $-252 \cdot 8^{\circ}$. It is but a few years since Onnes, after prolonged effort, secured sufficient helium to enable him to liquefy this gas too. In a brilliantly conceived research, he succeeded in accomplishing this feat in 1908, and in doing it reached a temperature within approximately 1° or 2° of the absolute zero.

The amount of liquid helium which Onnes obtained in his investigation was small, but it sufficed to enable him to show that a number of the elements possessed a remarkable " super-conductivity " at this low temperature. Mercury in particular, at the temperature of liquid helium, possessed an electrical conductivity ten million times greater than at ordinary room temperature, and currents started by induction in a coil of lead wire at the temperature of liquid helium maintained their intensity for more than an hour with but little diminution in magnitude.

The results obtained by Onnes, although limited in number, are of great importance, for they show that if liquid helium were rendered available in quantity, fundamental information of the greatest value on such problems as those connected with electrical and thermal conduction, with specific and atomic heats, with magnetism and the magnetic properties of substances, with phosphorescence, with the origin of radiation, and with atomic structure, could be obtained.

In spectroscopy, supplies of liquid helium would enable us to extend our knowledge of the fine structure of spectral lines, and thereby enable us to obtain clearer ideas regarding the electronic orbits existing in the atoms of the simpler elements. This would lead naturally to clearer views on the subject of atomic structure generally.

In other fields, too, important information could be obtained by the use of temperatures between that of liquid hydrogen and that of liquid helium. What of radioactivity? Would this property be lost by uranium, thorium, radium, and other similar elements at temperatures attainable with liquid helium? Would all chemical action cease at these temperatures? Would photochemical action disappear completely? Would photoelectric action cease or be maintained at such low temperatures?

In the fields of biological and botanical research, information on problems pressing for solution could be gained also. For example, would all life in spores and bacteria be extinguished by subjecting them to temperatures in the neighbourhood of absolute zero?

The list of problems rendered capable of attack by the use of liquid helium might be easily extended; but those cited already

will serve to show that the field is large, and that it is well worth while for us to make a special effort to secure adequate financial support for the equipment and maintenance of a cryogenic laboratory within the Empire.

It is probably beyond the ordinary resources of any university to equip and maintain such a laboratory ; but the project is one which merits national and probably imperial support.   It should appeal to private beneficence as well, for it is a project deserving strong and sympathetic help.

A properly equipped cryogenic laboratory should include:

(1) A liquid-air plant of large capacity.

(2) A liquid-hydrogen plant of moderate capacity.

(3) A liquid-helium plant of small capacity.

(4) Machine tools, cylinders, glass apparatus, measuring instruments, etc.

Such an equipment would probably cost more than £10,000.

For building purposes, probably an additional £10,000   or £15,000 would be required.

The staff should include one or two skilled glass-blowers, two or three mechanics and instrument makers, and two or three helpers for running the machinery.   To provide this staff and meet charges for light, heat, and power, probably £3,000 a year at least would be needed.

For an administrative and technical staff, probably £2,500 would be necessary.

In addition to the above, special provision would have to be made to secure an adequate supply of helium.   If industrial uses can be found for helium and a works were established in Alberta for the production of helium on a large scale, the problem of supply would be solved, for the amount of the gas which would be required for low-temperature research would probably not be more than 20,000 or 30,000 cubic feet a year.   In default of a production-works on a large scale being established, it would be necessary to instal a small plant at Calgary for the specific purpose of applying the cryogenic laboratory with helium.   This could easily e done at the present time, as the experimental plant is still 1 situ.   It would require from £3,000 to £4,000 to make the hanges in the plant which experience has shown are necessary nd to provide the additional auxiliary machinery, tools, etc., equired.

If this plant were run for three or four months each year, an dequate supply of helium could be obtained.   The expense of unning the plant under these conditions would be high, and it would probably be found that it would require from £2,000 to

£3,000 to operate it for a period of three or four months each year. This amount would, of course, have to cover charges for salary of staff, compensation to the owners of the natural gas, light, power, miscellaneous supplies, freight charges on cylinders, etc.

From the above it will be seen that a scheme such as that outlined would require in the aggregate a capital expenditure of about £30,000 for buildings and plant, and the interest on an endowment of about £125,000 for operating and maintaining the cryogenic laboratory together with the supply station.

If a cryogenic laboratory, with its auxiliary supply station, were established along the lines indicated, it would probably be found to be more economical to run the supply station continuously for a number of years, and to store for future use the helium accumulated. In this connexion it should be stated that the experimental plant as it exists would probably not produce more than 100,000 cubic feet of helium per year. The plant could, however, be easily manifolded, and the Governments of Great Britain and Canada might, from the point of view of national safety, legitimately be asked to assume responsibility for operating it.

Much of our knowledge acquired in the field of low temperature research we owe to the brilliant work of such distinguished men as Andrews, Davy, Faraday, and Dewar. The discovery of the rare gases, helium, neon, argon, krypton, and xenon, we owe to Rayleigh, Ramsay, and Dewar. How could we more fittingly perpetuate the work of these great men than by establishing on a permanent basis a cryogenic laboratory for the purpose of making still further progress in the field of low-temperature research—a field in which British scientists have made such brilliant and notable advances?

In conclusion, it should be stated that whilst the investigation just described was financed by the British Admiralty, and in its later stages by the British Air Ministry, valuable assistance was given by L'Air Liquide Société of Paris and Toronto, by the Canadian Pacific Railway Co. of Canada, by the Hydro-Electric Commission of Ontario, and by the University of Toronto. In carrying out the collateral investigations, valuable help was given by Professors E. F. Burton, J. Satterly, H. F. Dawes, and H. A. McTaggart. To Mr. J. Patterson, M.A., whose services were lent by the Director of the Meteorological Office of Canada, much credit is due for working out details of design and construction in connexion with the production of the rectifying column. Mention should also be made of the creditable manner in which the

experimental plant was handled during the trial runs made between December 1st, 1919, and April 17th, 1920, by Mr. R. J. Lang, assisted by Mr. D. S. Ainslie and Mr. H. R. Foreman.
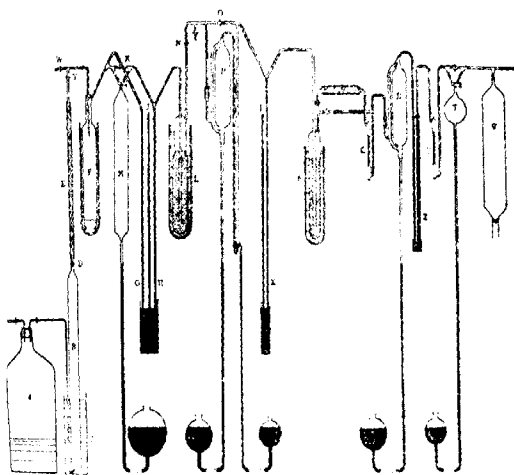
APPENDIX A.

Determinations of Helium Content of Natural Gases.

In determining the helium content of a sample of natural gas, the following procedure was adopted, and the apparatus used is shown in Fig. 2.

A is a glass bottle in which the gas was brought from the field. The gas was forced from *A* into the glass tube *B*, where it collected

FIG. 2.

by water displacement. The capacity of *B* was adjusted to be 1300 c.c. under ordinary conditions of temperature and pressure. The gas was introduced into the apparatus in units of this volume. Before commencing the analysis the charcoal tubes were strongly heated by electric heaters to about 300° to expel absorbed gases. and the whole of the apparatus to the right of the tap was carefully exhausted. All the taps were then turned off. The charcoal on cooling absorbed the remainder of the gas in apparatus. and a good vacuum resulted.

On turning the taps D and Y, the gas flowed from B through a drying tube E containing calcium chloride into the condenser F of about 400 c.c. capacity, which was immersed in liquid air kept in a Dewar's tube. Condensation of the hydrocarbons occurred at once, the liquid air boiling off rapidly. Comparison of the mano-meter G with the barometer J gave the pressure of the uncon-densed gases in F plus the vapour pressure of the condensed gases.

Usually B was filled and emptied five times in quick succession, so that the first charge in F was 6000 c.c. of natural gas. After some minutes when the liquid air had ceased from boiling and the manometer was at rest the pressure in F was read. Subtracting from this reading the vapour pressure of methane at the tempera-ture of liquid air, we get the pressure of the uncondensable gases in F, and knowing the volume of F it is an easy matter to find approximately the percentage of uncondensable gases in the sample of natural gas. This analysis, rough though it was, gave useful information as to the suitability of the natural gas for the manufacture of helium on a large scale.

Meanwhile, the tube L, of about 300 c.c. capacity, which was full of finely broken cocoanut charcoal, had been immersed in liquid air.

The tap K was then opened and the uncondensed gas shared between F and L. The mercury in the gauge rose quickly, and the liquid air surrounding L boiled vigorously, indicating a rapid evolution of heat when the gases are absorbed by charcoal. This was especially noticeable the first time the charcoal was used after being heated. When the gauges were nearly at the same level, K was closed, and the remainder of the uncondensed gas in F trans-ferred to L by means of the large mercury pump M. This pump was simply a long wide tube with a two-way tap at the top and a flexible tube and mercury reservoir at the bottom. It was very efficient, and after about five strokes practically all the gas had been transferred to L, the pressure in F falling to about 3 or 4 cm. The transfer of the gas was especially complete, since at each expansion of the matter in F some of the liquid methane would evaporate and sweep out the gas; an excess of pumping is detrimental, as it only transfers methane to L, thus tending to clog the charcoal. On standing, the pressure in L slowly decreased as absorption reached its maximum amount. Usually, very little except the helium was left unabsorbed in this tube.

When the reading of the gauge H was steady, the taps N and O were opened and the unabsorbed gas was allowed to diffuse over to a second charcoal tube S of about 200 c.c. capacity, which was also cooled in liquid air. The tap O was then closed, and com-

plete transference of the gas was effected by a mercury pump P of special design. In the early days of the experiment the pump in this position was of the same type as M, but the working and cleaning of the two-way tap proved inconvenient, and it was replaced by the pump shown.

While these operations had been going on any gas left in the apparatus between taps above S and the delivery tube was completely pumped out by the pump R, exhaustion being carried to such an extent that the electric charge had great difficulty in passing through the tube Q.

The gas having remained in the second charcoal tube S for some time and the gauge X attached to this tube having become steady, the taps above S were opened and the gas was pumped through the discharge tube and delivered to the collector Z, which was improvised from a graduated eudiometer by the placing of a tap at the closed end. The phosphoric oxide tube placed to the right of S was only required in the early stages of the experiment, when the charcoal gave off water on heating. A by-pass was placed in between S and the pump R to facilitate the action of the pump.

Before the gas was pumped off, its spectrum was carefully examined by a small, direct-vision spectroscope, and if any but the lines of helium (and mercury) were found, the gas was returned to the charcoal tube, or, in the case of great impurity, exhausted to the air and a fresh start made on a smaller quantity of the original gas. For example, if the natural gas contained large quantities of nitrogen and hydrogen, these may escape absorption, and their presence would be detected at this stage.

The gas obtained in the collector Z was invariably pure helium, and from the readings of its volume and pressure, the volume at atmospheric pressure was calculated.

Tubes similar to V were used for storage, and the pump T was designed to transfer the helium collected in Z over to V until the latter was filled at atmospheric pressure. The tube and pump had previously been exhausted by a mercury pump and a charcoal tube in liquid air (not shown in the figure), and then sealed off just to the right of V.

In making accurate determinations of the helium content of a natural gas, it was found necessary to use, for displacement purposes only, water which had been freed by boiling from occluded air and other gases. Ordinary tap-water or water from rivers was generally found to contain sufficient quantities of air to invalidate the determinations if high accuracy was demanded.
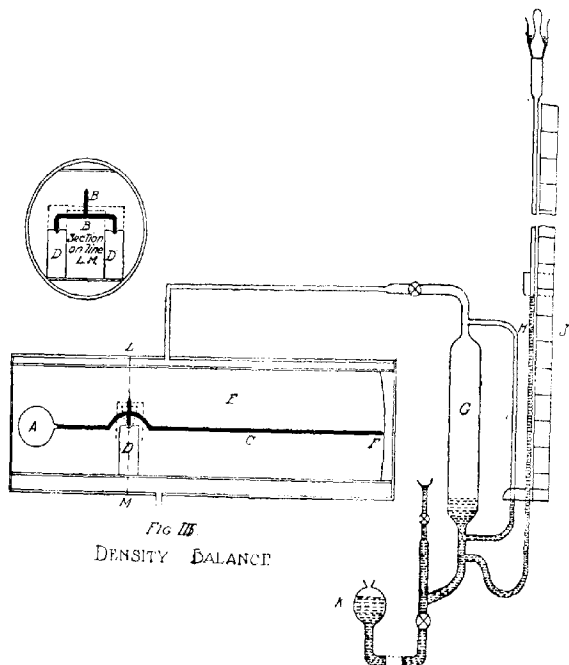
APPENDIX B.

Density Determinations by Balance Method.

For rapid and accurate determinations of gas density, the use of a delicately pivoted silica balance was found to be invaluable. This type of balance was originally designed and used by Aston

FIG. 3.

Fig III
DENSITY BALANCE

(*Proc. Roy. Soc.*, 1913, [.4], **89**, 439). A quartz micro-balance of exceedingly high sensitivity had been designed by Steele and Grant (*ibid.*, 1909, [4], **82**, 580), and used by Gray and Ramsay (*ibid.*, 1910, **84**, 536) at an earlier date, and Taylor (*Physical Rev.*, 1917, [N.S.], **10**, 653) has recently published an account of a form of the instrument which enabled him to determine with great exactness the density of helium. Aston's form of the instrument was, however, found to be the most suitable for our purposes. One

method of using the instrument has been described already by
R. T. Elworthy (*Bulletin No.* 31, *Mines Branch, Dept. of Mines,
Canada,* 1920), and a second, which has been found very useful, has
been worked out for the present investigation by Mr. John
Patterson, M.A. It is shown in Fig. 3.

The density balance consisted of a quartz bulb, *A*, 1·25 cm. in
diameter, and an arm, *C*, about 10 cm. long, mounted on a rocking
arm, *B*. The two points of this arm rested on jewels, and the
arm had a protecting case around it, as shown by the dotted lines,
so as to prevent the balance from getting out of the jewels. The
end of the arm, *C*, was turned at right angles and moved along
a scale, which could be easily read to 0·1 mm. In most forms of
this instrument, the pressure in the density chamber is adjusted
by either exhausting or admitting the gas very slowly until the
correct pressure is obtained. This is usually a very troublesome
operation, and to overcome it, a reservoir, *G*, was attached to the
chamber, which permitted the pressure to be altered by simply
raising or lowering the mercury reservoir. The reservoir was pro-
vided with a manometer, *H*, with a scale, the zero of which could
be set on the lower limb of the manometer and the pressure read
directly to 0·1 mm. The manometer, *H*, could be used either for
pressures less than atmospheric, in which case the tube, *H*, was
free of air, or for pressures greater than an atmosphere, when the
seal at the top is taken out. The balance could be calibrated for a
standard gas, such as air, by plotting pressures against the scale
reading. Then, to obtain the density of a gas, all that was neces-
sary was to wash out the density chamber thoroughly and take two
or three readings at different parts of the scale. From these, the
relative density could be determined at once. It was not necessary
by this method to adjust the pressure until the indicating point
was at a fixed position. A reading correct to two decimal places
could be obtained with this instrument in about five minutes.
The temperature of the air used for calibrating the balance should,
of course, be known, and then, if the other determinations were
made at a different temperature, a correction could be applied.

Organic Chemistry.

Positive Halogen in Organic Compounds. Iodine in Di-iodoacetylene and Chloroiodoethylene. LLOYD B. HOWELL [with WILLIAM A. NOYES] (*J. Amer. Chem. Soc.*, 1920, **42**, 991—1010).—It is suggested that the reactivity of halogen substitution derivatives of acetylene is due to the quadrivalence of the carbon atom rather than to the presence of a bivalent carbon atom (Nef, A., 1898, i, 102), and also to the positive character of the halogen atom, also exemplified when halogen replaces hydrogen in amino-, imino-, or hydroxyl groups. In agreement with this, di-iodoacetylene is shown to be produced by the action of iodine monochloride on calcium carbide or copper acetylide, although acetylene itself gives α-chloro-β-iodoethylene (Plimpton, T., 1882, 392). Further, di-iodoacetylene is decomposed by neutral, more quickly by acid, solutions of potassium iodide, with formation of acetylene, iodine, and potassium hydroxide. Although nitrogen iodide is considered to contain positive iodine atoms (Chattaway, A., 1900, ii, 722), it could not be obtained from di-iodoacetylene by means of ammonia, but this is not surprising, since acetylene is iodinated by the iodide (Datta and Prosad, A., 1917, i. 332). The formation of hexachloroethane by the action of chlorine on di-iodoethylene (Biltz, A., 1897, i, 389) is preceded by the production of the very unstable compound, $C_2Cl_4I_2$, yellow needles, which apparently melt, but probably decompose, at 42—43°. It decomposes in the dark, even at temperatures below 0°, within a few minutes, giving as-dichlorodi-iodoethylene, iodine trichloride, and traces of a liquid, b. p. 80—84°/32 mm., probably trichloroiodo-ethylene. This result, the formation of di-iodoacetylene by the action of alcoholic potash, and the fact that the whole of the iodine is not converted into iodide by treatment with lime or sodium peroxide, indicate that the compound is *αβ-dichloro-β-iodoethylene a-iododichloride*, CICl:CCl·ICl₂. *s-Dichlorodi-iodoethylene*,

$$CICl:CICl,$$

is an odourless, pale yellow liquid, b. p. 127·5—128·5°/25—26 mm., or 243·5° (corr. decomp.)/760 mm., which solidifies slightly below 0°. It reacts with difficulty with hot alcoholic silver nitrate solution, and gives di-iodoacetylene when treated with alcoholic potash. With chlorine, it gives an *iododichloride*, CICl:CCl·ICl₂, a yellow compound, which liberates one molecular proportion of iodine from potassium iodide. The course of the chlorination of di-iodo acetylene is therefore represented as follows: $C_2I_2 \longrightarrow$ |CEC·ICl₂| → CICl:CCl·ICl₂ → |CICl₂·CICl₂| → $C_2Cl_6 + 2ICl$. α-Chloroethylene β-iododichloride is produced by passing acetylene through a solution of iodine trichloride in hydrochloric acid; freshly crystallised from methyl alcohol, it melted at

i

66° (decomp.), but after several hours at 80°. Contrary to the statement of Thiele and Haakh (A., 1909, i, 865), its decomposition does not result in the formation of chlorine, but of iodine, iodine monochloride, and a number of liquid halogen compounds, of which the chief is $\alpha\beta\beta$-trichloro-α-iodoethane; no trace of as-chloroiodo-ethylene could be discovered. Iodine trichloride as usually prepared contains a large quantity of the monochloride. A very satisfactory method of preparing solutions of the trichloride in hydrochloric acid consists in the addition of a finely ground mixture of iodic acid (3 mols.) and re-sublimed iodine (1 mol.) to a cooled solution of twice the theoretical volume of hydrochloric acid (D 1·19). Such solutions may be kept indefinitely, even at 30°. The positive character of the iodine atom in nitrogen tri-iodide is illustrated by the formation of iodine monochloride on addition of concentrated hydrochloric acid to the tri-iodide.   J. K.

Vapour Composition of Mixtures of Ethyl Alcohol and Water. W. K. LEWIS (*J. Ind. Eng. Chem.*, 1920, **12**, 496—499).— The vapour composition of mixtures of ethyl alcohol and water was determined by Vrevski (A., 1912, ii, 1139) under varying pressures at 40°, 55°, and 75°. These results have been recalculated and extended by extrapolation up to the boiling points of the liquids. The vapour composition curve is shown diagrammatically, whilst the change in the vapour composition with the alteration in the boiling point has been determined from the slope of the temperature curves and plotted in a diagram, so as to be applicable to pressures other than the atmospheric pressure. The total pressure exerted by a given mixture of ethyl alcohol and water at a given temperature, divided by the pressure of pure water at the same temperature, forms a ratio which changes but little with a change in the temperature. The value of this ratio rises rapidly from water (as unity) with each increase of alcohol to about 2·3 for pure ethyl alcohol. The value of this ratio at the boiling point is plotted as a separate curve to enable the relationship between pressure and temperature to be made under other conditions than atmospheric pressure, as, for example, in the lower part of a rectifying column.   C. A. M.

The Ceryl Alcohol and Cerotic Acid of Chinese Wax. ALBERT GASCARD (*Compt. rend.*, 1920, **170**, 1326—1328).—Ceryl cerotate, as isolated from Chinese wax and carefully purified, has m. p. 84°. When hydrolysed, the ceryl alcohol obtained therefrom has m. p. 80°, and gives an iodide, m. p. 59°. Analysis of the iodide and the behaviour of the iodide when treated with sodium amalgam confirm Brodie's formula, $C_{27}H_{55}\cdot OH$, for this alcohol. Similarly, the cerotic acid, m. p. 82·–82·5°, isolated from the products of hydrolysis, is shown to have the formula $C_{26}H_{53}\cdot CO_2H$.   W. G.

Catalytic Preparation by the Dry Way of certain Ethers ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], 27, 328—330. Compare this vol., i, 6, 284).—When allyl alcohol

vapour is passed over calcined alum at 185—190°, a 30% yield of allyl ether is obtained. When the allyl alcohol is mixed with methyl alcohol or its four higher homologues, a certain amount of the mixed ethers is obtained, but the main product is allyl ether; in no case, however, is any appreciable amount of methyl ether or its homologues obtained. Under similar conditions, benzyl alcohol did not give benzyl ether, but a yellow, resinous compound, $(C_7H_6)_n$, but when the benzyl alcohol was mixed with methyl or ethyl alcohol, some mixed ether resulted. W. G.

Decomposition of Nitric Esters. ROBERT CROSBIE FARMER (T., 1920, **117**, 806—818).

The History of Zeise's Mercaptan and its Name. O. ZEISE (*J. pr. Chem.*, 1919, [ii], **100**, 48).—A personal note arising from Diergart's recent communication (this vol., i, 137) under the above title. H. W.

Crystallographic Properties of Sulphonal. H. SEIFERT (*Centr. Min.*, 1920, 97—101).—Sulphonal (diethylsulphondimethylmethane), $CMe_2(SO_2Et)_2$, crystallises in the monoclinic system, and is pseudo-rhombic in character; $a:b:c = 1.563:1:1.416$, $\beta = 90°31\frac{1}{2}'$. Crystals were examined grown from water, aqueous alcohol, ether, ethyl acetate, chloroform, carbon tetrachloride, and toluene; the habit of the crystals varies considerably according to the solvent from which they are grown. The crystals are generally well developed polyhedra, but from toluene or alcohol skeleton crystals are frequently obtained. Striations and vicinal faces sometimes appear. There is a good cleavage parallel to $a\{100\}$, and the crystals show considerable plasticity. They are colourless and show negative double refraction, the optic axial plane being $b\{010\}$. E. H. R.

n-Butyl Chloroformate and its Derivatives. FREDERICK DANIEL CHATTAWAY and ÉDOUARD SAERENS (T., 1920, **117**, 708—711).

The Use of αβ-Dichlorovinyl Ethyl Ether for the Production of Chloroacetates and Acid Chlorides. HOLLAND ROMPTON and PAULE LAURE VANDERSTICHELE (T., 1920, **117**, 91—693).

Leucic [a-Hydroxy*iso*hexoic] Acid and Walden's Inversion l Leucic Acid. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1919, **0**, 825—862).—Certain amino-acids, for example, glutamic acid and its salts, are extensively used in Japan as taste-promoting substances in food. The author has obtained very sweet substances by de-aminising leucine. Crude leucine hydrochloride, prepared by the hydrolysis of protein, is dissolved in several volumes of water and de-aminised; calcium oxide precipitates crude calcium a-hydroxy*iso*hexoate, which is suspended in water and treated with

sodium hydrogen carbonate, the filtrate giving sodium α-hydroxy-*iso*hexoate, long plates (from alcohol), after concentration. This salt as well as the ammonium, potassium, sodium hydrogen, potassium hydrogen, and calcium salts, is exceedingly sweet, being about ten times sweeter than sucrose. Since all the salts and the acid in dilute solution are sweet, whilst the solid acid and its ester are not, the taste must be due to the α-hydroxy*iso*hexoic ion. Neither Cohen's dulcigann nor Oertly and Meyer's glucophore is present in the α-hydroxy*iso*hexoic acid molecule. Its use is recommended as a substitute for calcium lactate or "saccharin."

The influence of substituents on the sweetness has also been investigated. Both the anhydrides, $C_4H_9 \cdot CH \underset{O \cdot CO}{\overset{CO \cdot O}{<}} CH \cdot C_4H_9$ and $C_4H_9 \cdot CH(OH) \cdot CO \cdot O \cdot CH(CO_2H) \cdot C_4H_9$, are bitter, but become sweet by boiling with alkalis. The acetyl derivative tastes like ether; its calcium salt is tasteless, but becomes sweet at 100°, owing to the formation of calcium α-hydroxy*iso*hexoate. Alkyl-leucic acids and their salts resemble the acetyl derivative.

The author has found that *d*-glutamic acid is twice as sweet as the *dl*-acid, and also that the sweetness of a metallic α-hydroxy*iso*hexoate becomes more pronounced the less the lævorotation of the salt. In accordance with this, *d*-α-hydroxy*iso*hexoic acid, prepared from the *l*-acid by Walden's inversion, gives *d*-salts, which are sweetest of all; the *dl*-acid, which is also produced during the inversion, is sweeter than the *l*-acid.

The following substances are described. l-α-*Chloroisohexoyl chloride*, b. p. 59° 11 mm., is slightly lævorotatory; in benzene solution its rotation approaches zero, and then becomes dextrorotatory by further dilution. l-α-*Chloroisohexoic acid* has b. p. 113·5--114° 10 mm., and $[\alpha] -19\cdot8°$ in 5% alcoholic solution; the ethyl ester has b. p. 79--80° 10 mm. and $[\alpha] -18\cdot4°$, and the anilide, needles, decomposes at 95--96°.. *Sodium* l-α-*hydroxyisohexoate* has $[\alpha] -25\cdot3°$, the *potassium* salt, m. p. 72°, has $[\alpha] -21\cdot6°$, and the *sodium hydrogen* salt,

$$C_6H_{11}O_3Na, C_6H_{12}O_3, 2H_2O,$$
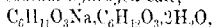
has $[\alpha]^{20} -28\cdot0°$ (tungsten light).   CHEMICAL ABSTRACTS.

Action of Heat on Oxalic Acid and Oxalates. G. CALCAGNI (*Gazzetta*, 1920, **50**, i. 245--251).—Hydrated oxalic acid melts at 98° and yields a mixture of carbon monoxide and dioxide, but not in equal volumes, at 110--120°. The anhydrous acid cannot be obtained by keeping the hydrated acid at a temperature somewhat above 100°, as the acid then sublimes and decomposes. Storage of the hydrated acid for several months in a vacuum desiccator over sulphuric acid yields an anhydrous compound, which begins to become pasty and to decompose at 135°, complete fusion and vigorous decomposition and distillation occurring at 160°. The melting point, given as 186--187° by Staub and Smith and as 189·5° by Althausen and Bamberger, could not be confirmed. The products yielded when various oxalates are decomposed by heat have also been investigated. [See *J. Soc. Chem. Ind.*, 1920, 501a.

T. H. P.

Preparation of Formaldehyde. MOYER DELWYN THOMAS (*J. Amer. Chem. Soc.*, 1920. **42**, 867—882).—The oxidation of methyl alcohol to formaldehyde by passing a mixture of air and methyl alcohol vapour over spirals of copper, silver, and gold, respectively, at 400° has been investigated. It is shown that silver is a more active catalyst than copper or gold in the dehydrogenation of methyl alcohol, and at the same time it produces less decomposition of the formaldehyde, so that the yield of formaldehyde is very much greater with silver than with gold or copper. With silver, an absolute yield of 95% and a process yield of 55·6% were obtained when the reaction mixture contained 0·25 gram of oxygen per gram of alcohol. Under similar conditions with gold, the absolute yield was 90·5%, and the process yield 50·5%, whilst the values for copper were 88·5% and 40% respectively. The best process yields were obtained with silver and gold, when the reaction mixture contained 0·4—0·5 gram of oxygen per gram of alcohol. With copper, this value was higher, 0·55—0·65 gram of oxygen per gram of alcohol. The optimum speed of the air for all three catalysts was 125- 150 litres per hour. The length of the catalyst spiral did not exert a very marked influence on the process. The temperature of the reaction was measured for gold, and found to vary between 520° and 900°, according to the conditions, although the spiral was only heated to 400° to start the reaction, and then the heating was stopped. Using gold, 1·7% of acetone or 10% of water in the alcohol did not appreciably influence the process. The process consists in dehydrogenation, followed by the oxidation of hydrogen and carbon monoxide.   J. F. S.

Physico-chemical Studies of Mixtures of Water, Acetaldehyde, and Paracetaldehyde. PAUL PASCAL and DUPUY (*Bull. Soc. chim.*, 1920, [iv], **27**, 353 362). The authors have etermined the solubility of paracetaldehyde in water, and of water i paracetaldehyde over the temperature range 0 80°, and have nown that the solubility of paracetaldehyde in water is much iminished by the presence of 5% of sulphuric acid. The relative olubility of acetaldehyde in paracetaldehyde and in water increases ith rise in temperature, and still further increases if sulphuric cid is present in the water.

Finally, the authors have determined the densities (D$^x_4$ and D$^x_4$) i paracetaldehyde and mixtures of paracetaldehyde and water, acetaldehyde and water, and acetaldehyde and paracetaldehyde in varying proportions.   W. G.

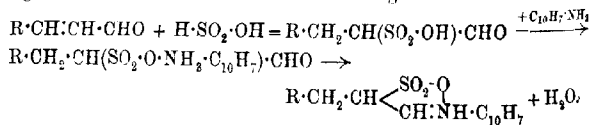**Action of Hydrocyanic Acid on Dextrose ; Kiliani's Reaction.** J. BOUGAULT and J. PERRIER (*Compt. rend.*, 1920, **170**, 1186—1189).—The combination of hydrogen cyanide with dextrose to give ammonium glucoheptonate does not take place in a feebly acid medium. A trace of alkali is sufficient to start the action, which is then continuous.

$$C_6H_{12}O_6 + KCN + 2H_2O = C_6H_{13}O_6 \cdot CO_2K + NH_3$$
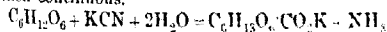
It is shown that the action of potassium cyanide on dextrose is bimolecular. W. G.

Purification of Celluloses. Action of Alkaline Earths on their Incrustations and on Hydro- and Oxy-celluloses. CARL G. SCHWALBE and ERNST BECKER (*J. pr. Chem.*, 1919, [ii], **100**, 19—47).—The action of the hydroxides of calcium, strontium, and barium, and of magnesium oxide on a number of hydro- and oxy-celluloses has been investigated, the actions generally being carried out at the boiling point of the solutions at the ordinary pressure. The authors are led to the following conclusions. Hydro- and oxy-celluloses are mixtures of celluloses and their degradation products. In the case of the hydrocelluloses from cotton or from wood, the latter are present in amounts of about 24—36%. Bleaching powder oxycellulose contains about 60% of pure cellulose and 40% of apparently oxidised degradation products. Sulphite celluloses contain cellulose dextrins, either naturally or formed during the process of boiling, which can be removed by boiling with lime. A variety of cellulose which is practically without reducing power is obtained by the action of boiling milk of lime on all sulphite celluloses, hydro- and oxy-celluloses. Sulphite wood celluloses lose up to 50% of their pentosan content when boiled with lime, whilst also the methyl content is depressed, sometimes to a considerable extent; the residue, however, still retains pentosans in very stable combination. Treatment with lime removes but little from soda wood celluloses, since any cellulose dextrins which may be present are dissolved during the boiling with alkali. [See, further, *J. Soc. Chem. Ind.*, 1920, July.] H. W.

Lignin and Reactions of Lignin. PETER KLASON (*Ber.*, 1920, **53**, [*B*], 706—711. Compare this vol., i, 148).—Further examination of β-naphthylamine lignosulphonate leads the author to ascribe to it a constitution different to that previously given, since it is now shown that only a portion of the β-naphthylamine is precipitated when the salt is gently warmed with dilute alkali, and that the salt is readily regenerated by the addition of β-naphthylamine hydrochloride to the filtered solution. The formation of the salt is considered to indicate the presence of the group R·CH:CH·CHO in lignin, and reaction is formulated according to the scheme

$$R·CH:CH·CHO + H·SO_2·OH = R·CH_2·CH(SO_2·OH)·CHO \xrightarrow{+C_{10}H_7·NH_2}$$

$$R·CH_2·CH(SO_2·O·NH_2·C_{10}H_7)·CHO \longrightarrow$$

$$R·CH_2·CH\begin{matrix} SO_2·O \\ CH:NH·C_{10}H_7 \end{matrix} + H_2O,$$

The compound is thus an internal ammonium salt in which the opening of the ring under the influence of alkali can occur in either of two directions, yielding either the alkali salt of the acid, R·CH_2·CH(·CH:N·C_{10}H_7)·SO_3H, or the alkali salt of lignin-sulphonic acid and free β-naphthylamine. The salt is formed in

greater quantity from old than from fresh sulphite liquors, so that it would appear that the group $R \cdot CH:CH \cdot CH_2 \cdot OH$ is present in the latter, and that the aldehyde is gradually formed in them by atmospheric oxidation.

The simplest aromatic substances containing these groups are cinnamaldehyde and cinnamyl alcohol. The colorations given by the former with phloroglucinol and Wiesner's reagent closely resemble those obtained with lignin. Also, when it is treated with the sulphite acid solution at 100° and the "reversible" sulphite is removed, the residual solution readily yields the cyclic salt,

$$CH_2Ph \cdot CH \underset{CH:NH \cdot C_{10}H_7}{\overset{SO_2 \cdot O}{<}},$$
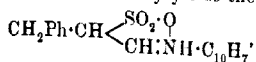
on treatment with β-naphthylamine hydrochloride, the properties of which are strikingly similar to those of β-naphthylamine lignin-sulphonate.

A consideration of these results and of others obtained by himself and different investigators leads the author to the conclusion that a hypothetical coniferylaldehyde (and coniferyl alcohol) are the most important and sole chemically active constituents, at any rate of coniferous lignin.

H. W.

Some Synthetic Peptides. (MLLE) L. PETRESCU (*Bul. Soc. Chim. România*, 1919, **1**, 56—60).—Phenylaminoacetic acid, when condensed with bromoacetyl chloride, yields *bromoacetylphenyl-glycine*, $CH_2Br \cdot CO \cdot NH \cdot CHPh \cdot CO_2H$, m. p. 140°, which, when treated with ammonia, gives *glycylphenylglycine*,

$$NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CHPh \cdot CO_2H,$$
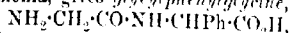
m. p. 226°, giving a *copper* salt and an anhydride, 3:6-*diketo-2-phenylpiperazine*, $CH_2 \underset{NH \cdot CO}{\overset{CO \cdot NH}{<}} CHPh$. m. p. 232°. W. G.

New Preparation of Amines by Catalysis. A. MAILHE (*Compt. rend.*, 1920, **170**, 1120—1123).—When the aldazines, obtained by the condensation of aldehydes with hydrazine, are passed together with hydrogen over reduced nickel at 140—160°, they do not yield symmetrical hydrazines, but the corresponding primary and secondary amines, the relative proportions of the two amines obtained varying with the temperature of hydrogenation and the aldazine used.

W. G.

Catalytic Hydrogenation of Ketazines. A. MAILHE (*Compt. rend.*, 1920, **170**, 1265—1267. Compare preceding abstract).—By hydrogenation with reduced nickel as a catalyst, the ketazines yield primary amines at low temperatures and a mixture of primary and secondary amines at higher temperatures. Thus dimethylketazine at 130—131° yields *isopropylamine*, and, in larger amount, *diiso-propylamine*. Diethylketazine, b. p. 160—163°, yields at 160—170° chiefly γ-*aminopentane*, $CH_3Me \cdot CH(NH_2) \cdot CH_2Me$, b. p. 84°, giving a *hydrochloride* and a *phenylcarbamide*, m. p. 148°. Diisopropyl-ketazine at 170—180° gives, as the chief product, γ-*amino-$\beta\delta$*.

dimethylpentane, $CHMe_2 \cdot CH(NH_2) \cdot CHMe_2$, b. p. 125—127°, giving a *phenylcarbamide*, m. p. 139—140°. Dipropylketazine at 170° gives δ-*aminoheptane*, $CH_2Me \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot CH_2Me$, b. p. 135—136°, giving a *hydrochloride* and a *phenylcarbamide*, m. p. 134°. Diisobutylketazine at 215—220° yields δ-*amino*-βζ-*dimethylheptane*, $CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot CHMe_2$, b. p. 175—177°, together with some *di-diisobutylcarbinylamine*,

$$[(CHMe_2 \cdot CH_2)_2 \cdot CH]_2NH.$$

W. G.

The Acylation of Thiocarbamides. AUGUSTUS EDWARD DIXON and JOHN TAYLOR (T., 1920, **117**, 720—728).

New Methods of Synthesis of Nitriles by Catalysis. ALPHONSE MAILHE (*Ann. Chim.*, 1920, [ix], **13**, 183—228).— A résumé of work already published (compare A., 1917, i, 686; 1918, i, 68, 105, 256, 336, 389, 532; this vol., i, 224, 377, 378, 380). W. G.

Electrolytic Preparation of Potassium Ferricyanide. O. W. BROWN, C. O. HENKE, and I. L. MILLER (*J. Physical Chem.*, 1920, **24**, 230—237).—The electrolytic oxidation of potassium ferrocyanide has been investigated. Using an undivided cell with electrodes of various shapes and with stirred and non-stirred solutions, the maximum yield was about 50%. When a diaphragm was used with a current density of 0·90 amp. per sq. dcm., potassium hydroxide was found in both compartments of the cell, and a current efficiency of about 98% was obtained. The presence of potassium hydroxide increases the current efficiency and decreases the voltage slightly. By leaving a space in the electrolysis vessel and operating a stirrer above the gauze anode, the ferricyanide can be forced below the electrode, where it crystallises, instead of on the anode, where it would cause voltage losses. All the ferrocyanide decomposed is not converted into ferricyanide. Different current efficiencies are obtained with different electrode materials, and in all cases the maximum current efficiency is reached when the electrolysis has been in progress for about four hours. The following maximum current efficiencies were obtained, working with an anode 7¼ cm. × 11½ cm. and a current of 0·95 amp.: copper 96·3%, nickel 97·7%, platinum 96·6%, Acheson graphite 99·7%, and lead covered with lead dioxide 93%. J. F. S.

Action of Hydrazine Hydrate on Glycerides of Higher Fatty Acids. I. P. FALCIOLA (*Gazzetta*, 1920, **50**, i, 162—165. Compare Falciola and Mannino, A., 1915, i, 59).—The action of hydrazine hydrate on triolein, tristearin, and various other derivatives of oleic and stearic acids yields compounds which correspond perfectly in their chemical and physical properties with the hydrazides studied by Curtius (A., 1896, i, 34, and elsewhere), and rapidly reduce Fehling's solution and ammoniacal silver nitrate solution. Further, the double linking of the oleic acid residue

appears to undergo hydrogenation during the action of the hydr-
azine hydrate, the compounds obtained from triolein and tristearin
exhibiting the same melting point, which remains unaltered when
the two compounds are mixed in various proportions. The identity
of the two compounds is not definitely established, but they exhibit
similar cryoscopic behaviour in p-nitrobenzaldehyde and similar
ebullioscopic behaviour in benzene; further, the hydrazide obtained
from triolein does not respond to the ordinary reactions for
compounds with a double linking in the molecule.

The *hydrazide*, $C_{17}H_{35}\cdot CO\cdot NH\cdot NH_2$, obtained from tristearin,
forms white leaflets, m. p. 115°, and that from triolein, white
leaflets, m. p. 114·5—115°. Similarly, ethyl oleate yields a com-
pound, m. p. 114—115°, and ethyl chloro-oleate or chlorostearate
a compound, m. p. 111—114°.

With zinc and acetic acid, the two hydrazides yield a crystalline
product of lower melting point, with permanganate in acetic acid
a white *compound*, m. p. (crude) 70—76°, and with sulphuric and
nitric acids together a *compound*, m. p. (crude) 55—60°.

T. H. P.

The Production of Ethylarsinic Acid. AMAND VALEUR and
RAYMOND DELABY (*Bull. Soc. chim.*, 1920, [iv], **27**, 366—370).—
The authors have repeated Dehn's work on the action of ethyl
iodide on tripotassium arsenite in alcoholic solution (compare A.,
1906, i. 341), and find that the action is much slower and less com-
plete than is stated by that author. The ethyl iodide disappears
much more rapidly than corresponds with the amount of arsenite
converted into ethylarsinate. If the action is carried out in aqueous
solution, there is not this loss of ethyl iodide, and the action is
fairly complete at the end of twenty-five days. W. G.

New Mercury Compounds obtained by the Oxidation of
Hydrazines by Mercuric Oxide. OTTO DIELS and SIBYLLE
UTHEMANN (*Ber.*, 1920, **53**, [*B*], 723—731). When an aqueous
solution of ethyl hydrazinecarboxylate is treated with yellow
mercuric oxide without precautions being taken to moderate the
temperature, an energetic action occurs, and large volumes of gas
are evolved, consisting mainly of nitrogen, but containing also
carbon monoxide and small quantities of an odoriferous substance,
hich is probably ethyl azidoformate; the aqueous solution con-
ains ethyl hydrazodicarboxylate, m. p. 130°, and a beautifully
rystalline mercury salt, $C_6H_8O_4N_2Hg$, needles, m. p. 155°. The
ormula $CO_2Et\cdot N(Hg\cdot CO_2Et)\cdot N(Hg\cdot CO_2Et)\cdot CO_2Et$ is assigned to
he latter, since it is decomposed by hydrochloric acid into mercuric
hloride, ethyl hydrazodicarboxylate, carbon monoxide, and
alcohol; by bromine in benzene solution into mercuric bromide,
ethyl azodicarboxylate, and ethyl bromoformate, and by piperidine
into mercury, ethyl hydrazodicarboxylate, and piperylurethane
(ethyl piperidine-*N*-carboxylate). Methyl hydrazinecarboxylate
reacts with yellow mercuric oxide in a precisely similar manner,

t

yielding methyl hydrazodicarboxylate and the mercury salt, $CO_2Me \cdot N(Hg \cdot CO_2Me) \cdot N(Hg \cdot CO_2Me) \cdot CO_2Me$, m. p. 215°.

The authors consider that their experiments lend some support to the hypothesis that di-imide or its derivatives are the primary products of the oxidation of hydrazines. In the present instance, they suppose that ethyl di-imidecarboxylate is first formed, $NH_2 \cdot NH \cdot CO_2Et + HgO = H_2O + Hg + NH \dot{:} N \cdot CO_2Et$, which further reacts with mercuric oxide to yield the mercury salt,

$$Hg(N \dot{:} N \cdot CO_2Et)_2.$$
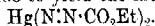
The latter then exhibits the tendency common to many simply substituted hydrazines of passing into symmetrical disubstituted derivatives, and yields the product,

$$CO_2Et \cdot N \dot{:} N \cdot Hg \cdot N(CO_2Et) \cdot N(CO_2Et) \cdot Hg \cdot N \dot{:} N \cdot CO_2Et,$$
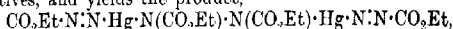
which in the manner of a diazonium compound loses nitrogen and gives the mercury salt.   H. W.

Kinetics of the Chlorination of Benzene. F. BOURION (*Compt. rend.*, 1920, **170**, 1319—1321).—In the chlorination of industrial benzene in the presence of iron as a catalyst, the yield of monochlorobenzene increases with the velocity of chlorination. For a given time and a given concentration, the fraction of a molecule of benzene converted into monochlorobenzene is 8·5 times greater than the fraction of a molecule of chlorobenzene converted into *p*-dichlorobenzene. The yield of monochlorobenzene decreases slightly with rise in temperature.   W. G.

The Chlorination of *m*-Dichlorobenzene. S. C. J. OLIVIER (*Rec. trav. chim.*, 1920, **39**, 411—413).—The principal product of the chlorination of *m*-dichlorobenzene in the presence of aluminium chloride is 1:2:4-trichlorobenzene. The results obtained confirm those of Cohen and Hartley (T., 1905, **87**, 1364), but refute those of Mouneyrat and Pouret (compare A., 1899, i, 263).   W. G.

o-**Chlorodinitrotoluenes.** I. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW (T., 1920, **117**, 784—793).

Preparation of certain Iodo-compounds. CUTHBERT WILLIAM JAMES, JAMES KENNER, and WILFRID VICTOR STUBBINGS (T., 1920, **117**, 773—776).

p-$\beta\beta$-**Dimethylpropylbenzenesulphonic Acid and certain of its Derivatives.** ARTUR BYGDÉN (*J. pr. Chem.*, 1919, [ii], **100**, 1—18).—*a*-Phenyl-$\beta\beta$-dimethylpropane (A., 1913, i, 29) is converted by sulphuric acid containing 6% of sulphur trioxide into p-$\beta\beta$-*dimethylpropylbenzenesulphonic acid*, $CMe_3 \cdot CH_2 \cdot C_6H_4 \cdot SO_3H$, the yield being about 95%; the acid forms long, colourless leaflets or large rectangular plates ($+ 2H_2O$), which, when preserved over concentrated sulphuric acid, are transformed into the *monohydrate*, m. p. 142·2—144·2° in an open, 145·6—146·6° (corr.) in a closed, capillary. The constitution of the acid is deduced from its conversion into *p*-hydroxybenzoic acid by oxidation with chromic acid

in dilute sulphuric acid, and subsequent fusion of the product with sodium hydroxide, and by its oxidation by permanganate to p-sulphobenzoic acid. The following salts are described: *potassium*, $+H_2O$; *rubidium*, $+H_2O$; *caesium*, $+\frac{1}{2}H_2O$; *sodium*, $+2H_2O$; *lithium*, $+H_2O$; *calcium*, $+\frac{1}{2}H_2O$; *strontium*, $+2H_2O$; *barium*, $+3H_2O$; *magnesium*, $+7H_2O$; *zinc*, $+6H_2O$; *cadmium*, $+3H_2O$; *ferrous*, $+7H_2O$; *nickel*, $+8H_2O$; *cobalt*, $+8H_2O$ (?); *lead*, $+2H_2O$; *copper*, $+6H_2O$; *silver*, $+1H_2O$; *ammonium*, anhydrous; *methylammonium*, $+\frac{1}{2}H_2O$, m. p. about $225°$ after much softening at about $150°$; *ethylammonium*, m. p. $114--115°$ (corr.) after previous softening; *brucine*, m. p. $211\cdot0--212\cdot0°$ (corr.). *p-ββ-Dimethylpropylbenzenesulphonyl chloride* forms colourless, rectangular plates or prisms, m. p. $58\cdot7--59\cdot2°$ (corr.), whilst the corresponding *bromide*, plates, has m. p. $65\cdot5--66°$ (corr.). The sulphonyl chloride is converted in the usual manner into the *amide*, needles, m. p. $101°$ (corr.), the *methylamide*, rhombic plates, m. p. $94\cdot8--95\cdot3°$ (corr.), the *anilide*, monoclinic plates, m. p. $137°$ (corr.), the *methylanilide*, colourless needles, m. p. $97\cdot8--98\cdot0°$ (corr.), the o-*toluidide*, thin, shining leaflets, m. p. $156--157°$ (corr.), the p-*toluidide*, rhombic plates, m. p. $117\cdot9--118\cdot2°$ (corr.), and the *benzylamide*, six-sided plates or colourless needles, m. p. $141\cdot5--141\cdot7°$ (corr.). *p-ββ-Dimethyl-propylphenol*, $CMe_3 \cdot CH_2 \cdot C_6H_4 \cdot OH$, small needles, m. p. $118\cdot0--118\cdot2°$ (corr.), is obtained by fusing potassium p-ββ-di-methylpropylbenzenesulphonate with potassium hydroxide, and subsequent acidification of the product.

H. W.

Preparation of *p*-Phenylenediamine and Aniline from their corresponding Chlorobenzenes. ARMAND J. QUICK (*J. Amer. Chem. Soc.*, 1920, **42**, 1033--1042).—The catalytic influence of copper salts on the reaction between ammonia and chlorobenzene (D.R.-P. 204951) or *p*-dichlorobenzene (D.R.-P. 202171) is not connected with the formation of copper ammonium compounds, since nickel, cobalt, and zinc salts, which form similar compounds, have no influence. Cuprous are more effective than cupric salts, which probably only become effective when reduced, and water cannot be replaced by alcohol as a solvent in the reaction. The reaction with dichlorobenzene is best carried out above $200°$; with $5--6\%$ solutions of ammonia, the reaction is very incomplete, and an amorphous, red product is also produced. Addition of iron filings or activated charcoal to the cuprous salt improves the appearance of the final product, but with concentrated solutions of ammonia they, particularly the former, tend to retard the reaction. The action of ammonia on chlorobenzene under the conditions prescribed gave only a 39% yield, as against 80% claimed by the patent. Increase in concentration of ammonia beyond 14%, or in working temperature beyond $200°$, does not improve the yield, although the latter is necessary for complete decomposition of the chlorobenzene. Cuprous iodide has no catalytic value for this reaction. Diphenylamine could not be

obtained from bromobenzene under the conditions prescribed by D.R.-P. 187870.   J. K.

Nitration of Aceto-m-toluidide. JAMES WILFRED COOK and OSCAR LISLE BRADY (T., 1920, **117**, 750—753).

α-**Aminophenyl-α-naphthylmethane. I.** SERGIO BERLINGOZZI (*Gazzetta*, 1920, **50**, i, 215—221).—By reducing the two stereo-isomeric oximes of phenyl α-naphthyl ketone by means of zinc and hydrochloric acid, Poccianti (A., 1915, i, 822) obtained amino-phenyl-α-naphthylmethane hydrochloride, which agrees in proper-ties with the hydrochloride prepared by Busch and Leefhelm (A., 1908, i, 152) from magnesium α-naphthyl bromide and hydrobenz-amide. The latter authors give m. p. 121° for the corresponding free base, whereas the present author finds m. p. 56—59° for the base derived from Poccianti's hydrochloride. In the form-ation of the latter, the Beckmann transformation may possibly result in the change OH·N:CPh·C$_{10}$H$_7$ $\longrightarrow$ C$_6$H$_5$·CO·NH·C$_{10}$H$_7$, so that the base would then have the formula C$_{10}$H$_7$·NH·CH$_2$Ph instead of C$_{10}$H$_7$·CHPh·NH$_2$. That such change does not occur and that the base is actually a primary amine is shown by the facts that: (1) the same base is obtained when the oxime is reduced by means of sodium amalgam in acetic acid solution, (2) the action of nitrous acid converts the base into the corresponding alcohol, phenyl-α-naphthylcarbinol, (3) the base readily yields the corre-sponding p-hydroxybenzylidene derivative when treated with p-hydroxybenzaldehyde, and (4) benzoyl-α-naphthylamine.

C$_{10}$H$_7$·NHBz.
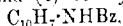
is not reduced by sodium amalgam.

α-*Aminophenyl-α-naphthylmethane*, C$_{10}$H$_7$·CHPh·NH$_2$, forms rosettes of long, colourless, prismatic crystals, m. p. 56—59°, and its *acetate*, shining, white scales, m. p. 119°. The p-*hydroxy-benzylidene* derivative, C$_{10}$H$_7$·CHPh·N:CH·C$_6$H$_4$·OH, crystallises in tufts of minute, acicular crystals, m. p. 235°.   T. H. P.

The Preparation of Picric Acid. Influence of the Degree of Sulphonation of the Phenol on the Yields of Trinitro-phenol. MAURICE M. DOLL (*Bull. Soc. chim.*, 1920, [iv], **27**, 370—374).—Other things being equal, the yield of trinitrophenol increases regularly with the degree of sulphonation of the phenol.
W. G.

Identification of Acids. V. p-Halogenophenacyl Esters. W. LEE JUDEFIND and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 1043—1055).—Certain of the phenacyl esters previously described (A., 1919, i. 157) are oils or solids of low melting point. It is now shown that derivatives with a convenient range of melt-ing points are, in general, easily obtained from p-halogenophen-acyl bromides. The esters of aspartic, maleic, racemic, tartaric, and mucic acids derived from p-bromo- and p-chloro-phenacyl bromides decomposed without melting, whilst the salts of linoleic,

oleic, oxalic, monochloroacetic, trichloroacetic, and formic acids did not react. A liquid ester was obtained from α-hydroxybutyric acid, and gallic acid gave only a small quantity of an unsatisfactory product. p-*Iodophenacyl bromide* (ω-*bromo*-p-*iodoacetophenone*), $C_6H_4I \cdot CO \cdot CH_2Br$, yellow crystals, m. p. 113·5°, is obtained by brominating p-iodoacetophenone. p-*Bromophenacyl alcohol*, $C_6H_4Br \cdot CO \cdot CH_2 \cdot OH$, m. p. 136·6°, and p-*iodophenacyl alcohol*, m. p. 152°, were obtained from the acetates by the action of barium carbonate. The following esters were prepared (the temperatures indicating melting points):

p-*Chlorophenacyl acetate*, 67·2°; *aconitate*, 169°; *benzoate*, 118·6°; *ethylglycollate*, 94·4°; *succinate*, 197·5°; *thiocyanate*, 135·2°; *tricarballylate*, 125·6°.

p-*Bromophenacyl acetate*, 85°; *aconitate*, 186°; *anisate*, 152°; *benzoate*, 119°; *butyrate*, 63·2°; *isobutyrate*, 76·8°; *decoate*, 66°; *hexoate*, 71·6°; *octoate*, 65·5°; *cinnamate*, 145·6°; *citrate*, 148°; *erucate*, 61°; *ethylglycollate*, 104·8°; *glycollate*, 138°; *hippurate*, 151°; β-*phenylpropionate*, 104°; *lactate*, 112·8°; *laevulate*, 84°; *margarate*, 78·2°; *palmitate*, 81·5°; *phenylacetate*, 89°; *propionate*, 59°; *pyromucate*, 138·5°; *salicylate*, 140°; *sebacate*, 147°; *sorbate*, 129°; *stearate*, 78·5°; *succinate*, 211°; *thiocyanate*, 116·5°; o-*toluate*, 56·9°; m-*toluate*, 108°; p-*toluate*, 153°; *tricarballylate*, 138·2°; *valerate*, 63·6°; *isovalerate*, 68°.

p-*Iodophenacyl acetate*, 114°; *benzoate*, 126·5°; *butyrate*, 81·4°; *isobutyrate*, 109·2°; *decoate*, 80°; *hexoate*, 81·5°; *octoate*, 77°; *isovalerate*, 78·8°; *erucate*, 73·8°; *lactate*, 139·8°; *margarate*, 88·8°; *palmitate*, 90°; *propionate*, 94·9°; *stearate*, 90·5°; *valerate*, 78·6°.

<div align="right">J. K.</div>

Polymerisation in Ethereal Solution by means of Ferric Chloride. Seventh Polymeride of Anethole. E. PUXEDDU (*Gazzetta*, 1920, **50**, i. 149 154. Compare A., 1913, i. 460; 1916, i. 806).—Addition of ethereal ferric chloride solution to an ethereal solution of anethole results in the immediate precipitation of a white substance; fractional distillation of the latter under reduced pressure yielding a new polymeride, the seventh known, of anethole. The author and Marica (A., 1916, i. 807) consider that eleven such isomeric polymerides are possible, although Orndorff and Morton (A., 1900, i. 289) maintain that phenols containing a propenylic chain are able to exist in only two isomeric forms. The author has prepared in the pure state the α-butenyl and p-iso-pentenyl-anisoles described by Moureu and Chauvet (A., 1897, i. 403), and has studied their bromides and polymerides.

The seventh *polymeride* of anethole, $(C_{10}H_{12}O)_x$, forms prismatic crystals, m. p. 132°; owing to lack of material, its molecular weight was not determined.

p-*Butenylanisole* has b. p. 245 248°, and yields a dibromide, which was not analysed, and, when treated with ethereal ferric chloride, a dense, oily polymeride.

p-*isoPentenylanisole* forms a colourless, faintly opalescent liquid,

b. p. 248—252°, n 1·54, with the odour of aniseed. The bromide (not analysed) forms long, slender needles, m. p. 93—95°, and the polymeride a dense, gummy mass.   T. H. P.

o-**Anisyltellurium Compounds.** KARL LEDERER (*Ber.*, 1920, **53**, [*B*], 712—716. Compare A., 1917, i, 134; this vol., i, 40).— Di-*o*-anisyl telluride has been prepared by the action of magnesium *o*-anisyl bromide on tellurium dibromide; it is purified by conversion into the crystalline dibromide, and reduction of the latter with magnesium methyl iodide.

Di-o-anisyl telluride, Te(C_6H_4·OMe)$_2$, is a colourless, crystalline substance, m. p. 73—74°, b. p. 248–251°/30 mm., which gives rise to the following *di-o-anisyltelluronium* compounds in the usual way: *dichloride*, microscopic rods, m. p. 184—185° after softening at 182°; *dibromide*, small, monoclinic platelets, m. p. 195—196° after softening at 192°; *di-iodide*, shining, metallic, iodine-coloured needles, m. p. 199—200° after softening at 198°; *oxide*,
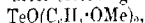
$$TeO(C_6H_4\cdot OMe)_2,$$

needles, m. p. 205—206°; *methiodide*, small rods, m. p. 124—125°. It also forms *additive* compounds with mercuric haloids, as follows: *iodide*, Te(C_6H_4·OMe)$_2$,HgI$_2$, yellow crystals, m. p. 80—81° after softening at 79°; *bromide*, yellow crystals, m. p. about 84° after softening at 70°; *chloride*, obtained as an oil, which, after solidification, has m. p. 143—144°, and after recrystallisation has m. p. 156—157° (decomp.) after softening at 150°.   H. W.

Relationship between Chemical Constitution and Physiological Action in Local Anæsthetics. I. Homologues of Procaine. OLIVER KAMM (*J. Amer. Chem. Soc.*, 1920, **42**, 1030—1033).—γ-*Diethylaminopropyl* p-*nitrobenzoate hydrochloride*, from *p*-nitrobenzoyl chloride and γ-diethylaminopropyl alcohol, m. p. 189—190°, on reduction with tin and hydrochloric acid gives γ-*diethylaminopropyl* p-*aminobenzoate*, m. p. 69° (*hydrochloride*, needles, m. p. 164°), which is structurally similar to cocaine, and in physiological action is intermediate between this drug and procaine (novocaine). It is slightly more toxic, but considerably more effective as a surface anæsthetic than the latter. γ-*Diethylaminopropyl* m-*nitrobenzoate hydrochloride*, m. p. 139—140°, yields γ-*diethylaminopropyl* m-*aminobenzoate*, a colourless oil, which solidifies only at a low temperature (*hydrochloride*, m. p. 151°).   J. K.

The Constitution of Acylanthranils. GUSTAV HELLER (*Ber.*, 1920, **53**, [*B*], 731—732).—A further contribution to the discussion on this subject (compare Heller and Lauth, this vol., i, 181; Schröter, this vol., i, 333). The author maintains his original views, and points out that the properties of the crystalline additive products of hydrazine and lactones differ considerably from those of the substances formed from hydrazine and acylanthranils, particularly from the point of relative stability.   H. W.

β-Halogenoethylaminobenzoic Esters. J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1334641).—*Ethyl p-β-chloroethylamino-benzoate*, $CH_2Cl \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2Et$, crystals, m. p. 69°, b. p. 183°/3 mm., is obtained by adding a solution of the corresponding hydroxy-compound (20 parts) in dry benzene (15 parts) to a mixture of phosphorus pentachloride (20 parts) and dry benzene (25 parts), heating the mixture on the water-bath, evaporating the benzene and phosphoryl chloride, and distilling the residue under reduced pressure. Dimethylaniline and thionyl chloride may be used instead of benzene and phosphorus pentachloride; in this case, the product of the reaction is treated with warm water, whereby dimethylaniline hydrochloride dissolves and the ester separates in granules. Other esters may be prepared similarly. They are useful as local anæsthetics. CHEMICAL ABSTRACTS.

β-Alkylaminoethylaminobenzoic Alkyl Esters. J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1334642).—*Ethyl p-β-diethylamino-ethylaminobenzoate*, $NEt_2 \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2Et$, an oil (hydrochloride, white needles, m. p. 156°), is obtained by heating a mixture of diethylamine (2 mols.) and ethyl *p-β-chloroethyl-aminobenzoate* (1 mol.) in a closed vessel for several hours at 100°, and treating the cooled, crystalline mass with water to dissolve diethylamine hydrochloride. The corresponding *butyl* ester has b. p. 213—214°/6 mm., and forms a *hydrochloride*, m. p. 127°. *Butyl p-β-methylaminoethylaminobenzoate*, b. p. 214°/6 mm., forms a hydrochloride, m. p. 141°. CHEMICAL ABSTRACTS.

Mechanism of the Reaction between Ketens and the Grignard Reagent. HENRY GILMAN and L. C. HECKERT (*J. Amer. Chem. Soc.*, 1920, **42**, 1010—1014).—Hitherto, all the reactions of the ketens have been attributed to initial addition to the ethylenic inking, but, on the other hand, no case is known in which the Grignard reagent combines directly with such linkings. By direct benzoylation of the initial product of the reaction between diphenyl keten and magnesium phenyl bromide, triphenylvinyl benzoate, $CPh_2 CPh \cdot O \cdot COPh$, was obtained, showing that addition of the Grignard reagent had taken place at the carbonyl group. J. K.

Iodination of the Phenoxyacetic Acids. EFISIO MAMELI, EVARISTO GAMBETTA, and GUIDO RIMINI (*Gazzetta*, 1920, **50**, i. 166—186).—Of the various methods tried for the iodination of phenoxyacetic acid and some of its substituted derivatives, the action of iodine in presence of iodic acid in chloroform solution is found to give the best results. The acids employed gave the following melting points, some of which differ slightly from those found in the literature: phenoxyacetic acid, 99—100°; 2-methoxy-phenoxyacetic acid, 123—125°; 3-methyl-6-isopropylphenoxyacetic acid, 147—148°; α-naphthoxyacetic acid, 190°; β-naphthoxyacetic acid, 156°.

p-Iodophenoxyacetic acid, $C_6H_4I \cdot O \cdot CH_2 \cdot CO_2H$, obtained by

iodinating phenoxyacetic acid, and also by the action of chloroacetic acid on *p*-iodophenol, crystallises in shining, colourless, odourless scales, m. p. 155—156°; at first it appears tasteless, but a persistent, sweet taste gradually develops. On nitration, it yields 4-iodo-3-nitrophenol. The *potassium, calcium* ($+2H_2O$), *silver,* and *copper* ($+2H_2O$) salts were prepared and analysed. The *ethyl* ester, $C_{10}H_{11}O_3I$, forms colourless, tasteless, rhombohedral plates, m. p. 62–63°, with a pronounced fruity odour. The *amide*, $C_8H_8O_2NI$, crystallises in silky, white needles, m. p. 165—166°.

5-*Iodo*-2-*methoxyphenoxyacetic acid*, $OMe \cdot C_6H_3I \cdot O \cdot CH_2 \cdot CO_2H$, prepared by iodinating 2-methoxyphenoxyacetic acid, and also by the action of chloroacetic acid on 5-iodo-2-methoxyphenol, forms slender, white, odourless, tasteless needles, m. p. 155°. By cold concentrated sulphuric acid it is coloured first violet and then brown, and afterwards charred; the sulphuric acid solution colours chloroform violet, and emits iodine vapour when heated. Similar behaviour is shown by the yellowish-brown solution obtained with concentrated nitric acid. The *potassium* and *silver* salts were prepared and analysed.

4-*Iodo*-2-*methoxyphenoxyacetic acid*, obtained from 4-iodo-2-methoxyphenol and chloroacetic acid, crystallises in white, nacreous scales, m. p. 83—84°.

4-*Iodo*-3-*methyl*-6-iso*propylphenoxyacetic acid*,
$$C_6H_2MePr^\beta I \cdot O \cdot CH_2 \cdot CO_2H,$$
prepared by iodination of 3-methyl-6-*iso*propylphenoxyacetic acid in *iso*amyl alcohol, and also by the action of chloroacetic acid on 4-iodo-3-methyl-6-*iso*propylphenol, crystallises in small, white, colourless, tasteless needles, m. p. 126—127°, and towards sulphuric and nitric acids behaves similarly to 5-iodo-2-methoxyphenoxyacetic acid. Its *potassium* and *silver* salts were prepared and analysed.

1-*Iodo*-β-*naphthoxyacetic acid*, $C_{10}H_6I \cdot O \cdot CH_2 \cdot CO_2H$, prepared by iodination of β-naphthoxyacetic acid, and also by the interaction of chloroacetic acid and 1-iodo-β-naphthol, forms thin, white, odourless plates. m. p. 170—171°. It becomes pale yellow at 138° and pink at 145°, the colour deepening as the melting point is approached; at 203—210° it decomposes, with emission of violet vapour. Concentrated sulphuric acid decomposes it, with evolution of violet vapour, the acid assuming a brown colour with green reflexion. In cold concentrated nitric acid it is insoluble, but the hot acid dissolves it, giving a ruby-red liquid and violet vapours. The *potassium* and *silver* salts were prepared and analysed.

Iodo-α-*naphthoxyacetic acid*, $C_{10}H_6I \cdot O \cdot CH_2 \cdot CO_2H$, prepared by iodination of α-naphthoxyacetic acid, forms slender, pink, odourless crystals, m. p. 168–170°, and decomposes, with evolution of iodine vapour, at 195°. It colours concentrated sulphuric acid violet-pink, and liberates iodine when treated with boiling concentrated nitric acid. No suitable iodo-derivative of α-naphthol being known, the position of the iodine in this acid could not be established. The *potassium* and *silver* salts were prepared and analysed.   T. H. P.

The Behaviour of Optically Active Esters on Hydrolysis.
ALEX. McKENZIE and HENRY WREN (T., 1920, 117, 680—690).

Case of Isomerism in the Series of Aromatic α-Ketonic
Acids. H. GAULT and R. WEICK (Compt. rend., 1920, 170,
1392--1395).—Ethyl phenylpyruvate as prepared by Bougault
(compare A., 1914, i, 839) and by Hemmerlé (compare A., 1915,
i, 78) is a solid, m. p. 45° (the present authors find m. p. 51--52°).
By the hydrolysis of ethyl cyanophenylpyruvate in alcoholic
medium, and fractional distillation of the crude product, an
isomeric ethyl phenylpyruvate is obtained as a liquid, b. p. 149°/
15 mm., which will not solidify. This liquid isomeride gives a
bisulphite compound, a semicarbazone, and a phenylhydrazone
identical with those from the solid isomeride. It is shown that
the solid isomeride is the unstable form, and that by slow distilla-
tion under reduced pressure it is converted into the stable liquid
form, but the change is not reversible. The new method of pre-
paration really gives a crude mixture of the two isomerides, which,
during the fractional distillation, is entirely converted into the
liquid form.
β-Hydroxy-α-phenylmaleinide was isolated as an intermediate
product of the hydrolysis of ethyl cyanophenylpyruvate.　W. G.

Synthesis of Bibasic Acids by the Action of Malonic
Acid on Hydrols. Replacement of the Hydroxy-group
by the Group ·CH(CO₂H)₂. R. FOSSE (Ann. Chim., 1920,
[ix], 13, 154--183. Compare this vol., i, 390 395).--A more
detailed account of work already published (compare A., 1906,
975; 1907, i. 414).　　　　　　　　　　　　　　W. G.

The Constitution of Some Dialkyl*cyclo*hexanones. R.
CORNUBERT (Compt. rend., 1920, 170. 1259 1262. Compare A.,
914, i, 969). A further study of the allyl derivatives obtained by
the action of allyl iodide on *cyclo*hexanone and the three methyl-
*cyclo*hexanones in the presence of sodamide by means of the action
of benzaldehyde (compare this vol., i, 390). The constitutions of
these compounds are 1-methyl-4 allyl*cyclo*hexan-2-one, giving a
benzylidene derivative, b. p. 211 212 15 mm. (corr.); 1-1-diallyl-
*cyclo*hexan-2-one, giving a *benzylidene* derivative, b. p. 231 232
18 mm. (corr.); 1-methyl-3:3 diallyl *cyclo*hexan-4 one with a
benzylidene derivative, d. p. 71 71.5 ; and 1-methyl-2:2(or
4:4)-diallyl*cyclo*hexane-3(or 5) one with a *benzylidene* derivative,
b. p. 45--48°. Similarly, other di and tri-alkyl *cyclo*hexanones
previously described (compare A., 1914, i, 251, 969) have the con-
stitution 1-methyl-1-*n*-propyl*cyclo*hexan-2 one and 1-methyl-1:3-
diallyl*cyclo*hexan-2-one.　　　　　　　　　　　　　W. G.

Acidylketimines. CHARLES MOUREU and GEORGES MIGNONAC
(Compt. rend., 1920, 170, 1353 1356). Organo-magnesium

derivatives of the type CRR':N·MgBr, obtained by the condensation of nitriles, RCN, with magnesium alkyl bromides, R'MgBr, react with acid chlorides to give acidylketimines, thus:

CRR':N·MgBr + R″COCl = CRR':N·COR″ + MgBrCl.
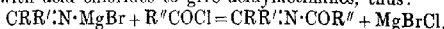
In this way, the authors have prepared *acetylphenylethylketimine*, CPhEt:N·COMe, m. p. 126°; *butyrylphenylethylketimine*, m. p. 85·5°; iso*valerylphenylethylketimine*, m. p. 117°; *benzoylphenylethylketimine*, m. p. 165°; *acetylphenyl*iso*butylketimine*, m. p. 134°; and *benzoylphenyl*iso*butylketimine*, m. p. 160°.

All these acidylketimines are hydrolysed by dilute mineral acids to give a ketone, an acid, and an ammonium salt,

CPhEt:N·COMe + 2H₂O + HCl = COPhEt + CH₃·CO₂H + NH₄Cl.

When hydrolysed by alkalis, they give the ketone, the alkali salt of the organic acid, and ammonia.   W. G.

The Stereoisomeric Forms of Benzoylphenylacetylene Di-iodide. CHARLES DUFRAISSE (*Compt. rend.*, 1920, 170, 1262—1264. Compare A., 1914, i, 845).—Nef (compare A., 1900, i, 20) obtained only one di-iodide by the action of iodine on benzoylphenylacetylene. By suitably modifying Nef's process, the author has obtained two stereoisomeric di-iodides. The substance *A*, m. p. 155—156°, is th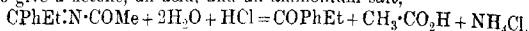e one described by Nef. The *di-iodide*, *B*, occurs in two distinct crystalline forms. *B*ₐ and *B*ᵦ. *B*ₐ is converted into *B*ᵦ when heated at its m. p., 82°; *B*ᵦ has m. p. 84—85°, and ·is converted into *B*ₐ by rapid cooling or rapid evaporation of its alcoholic solution.   W. G.

The Diphensuccindene Series. II. 2 : 2′-Dibenzoyl-benzil and its Derivatives. K. BRAND and H. LUDWIG (*Ber.*, 1920, 53, [B], 809—814).—The constitution assigned previously to the brown hydrocarbon, 9:12-diphenyldiphensuccindiadiene (A., 1912, i, 960), is confirmed by the observation that it is oxidised by chromic acid in hot glacial acetic acid solution, with the production of two molecules of o-benzoylbenzoic acid from each molecule of the hydrocarbon. If, however, the oxidation is carried out in cold solution, 2:2′-*di-benzoylbenzil*, C₆H₄Bz·CO·CO·C₆H₄Bz, yellow crystals, m. p. 188°. is obtained. The latter slowly condenses with o-phenylenediamine in boiling glacial acetic acid solution to yield 2:3-*di*(o-*benzoylphenyl*)-*quinoxaline* (annexed formula), colourless, silky crystals, m. p. 237—238°. 2:2′-*Di*-p-toluoylbenzil, yellow crystals, m. p. 191°, is similarly formed from 9:12-di-p-tolyldiphensuccindiadiene.   H. W.

The Diphensuccindene Series. III. Coloured Phenol Ethers of the Diphensuccindene Series. K. BRAND and F. W. HOFFMANN (*Ber.*, 1920, 53, [B], 815—821. Compare A., 1912, i, 960, and preceding abstract).—The action of magnesium o- and p-anisyl bromides on diphensuccindan-9:12-dione has been investigated, and a series of derivatives have been prepared which

are closely similar to the phenyl and *p*-tolyl compounds described previously.

8 : 12 - *Dihydroxy*-8 : 12-*di* - o - *anisyldiphensuccindane* (annexed formula) forms colourless, transparent needles, m. p. 207·5°, and is converted by a boiling mixture of glacial acetic and formic acids into 9 : 12 - *di-o-anisyldiphensuccindadiene*, reddish-brown needles, m. p. 247°. The latter is oxidised by a warm solution of chromic acid in glacial acetic acid to 2: 2′-*di-o-anisoylbenzil*, $OMe \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot CO \cdot CO \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot OMe$, pale yellow needles, m. p. 244°, which condenses with *o*-phenylenediamine to yield 2 : 3-*di*[*o-anisoylphenyl*]-*quinoxaline*, almost colourless needles, m. p. 250°.
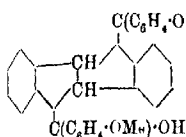
9 : 12-*Dihydroxy*-9 : 12-*di-p-anisyldiphensuccindane*, colourless, transparent needles, m. p. 230°, is readily dehydrated to 9 : 12-*di-p-anisyldiphensuccindadiene*, brown needles, m. p. 242°. (When the Grignard reagent is prepared from *p*-anisyl iodide, the diene is sometimes the only isolable substance.) It is converted by gentle oxidation with chromic acid in glacial acetic acid into *di-p-anisoyl-benzil*, yellow needles, m. p. 214°, whilst more drastic oxidation converts it into 2-*p*-anisoylbenzoic acid, m. p. 138° (the literature records m. p. 142—143°). The benzil condenses with *o*-phenylenediamine to yield 2 : 3-*di*(p-*anisoylphenyl*)-*quinoxaline*, almost colourless needles, m. p. 251°. H. W.

Constitution of Enols. IV. Enolisation of 2-Monoacylindane-1 : 3-diones.

JOHANNES SCHEIBER and GEORG HOPFER (*Ber.*, 1920, **53**, [*B*]. 697—706). The enolisation of monoacylindanediones may occur in such a manner as to yield products of the formula (i) $C_6H_4 \diagdown \begin{matrix} C(OH) \\ CO \end{matrix} > CR \cdot OR$ or

(ii) $C_6H_4 \diagdown \begin{matrix} CO \\ CO \end{matrix} > CCR \cdot OH$.
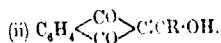
The authors have therefore investigated the behaviour of ethyl 1:3-diketohydrindene-2-carboxylate, 2-acetyl- and 2-benzoyl-1:3-diketohydrindenes towards ozone, and in each case find that enolisation occurs, at any rate to some extent, so as to give rise to substances of the second formula.

The main products of the action of ozone on a solution of ethyl 1:3-diketohydrindene-2-carboxylate in carbon tetrachloride at −20° are phthalic acid and ethyl glyoxalate, which can only be derived from an enol of type (i); at the same time, considerable quantities of carbon dioxide are formed, the bulk of which is attributable to the decomposition of ethyl hydrogen carbonate, whilst smaller quantities arise from the oxidation of triketohydrindene to phthalic acid, thus indicating that enolisation also occurs in such a manner as to yield type (ii). Ozonisation of 1:3 diketo-

2-acetylhydrindene must produce either phthalic acid and methyl glyoxal or triketohydrindene and acetic acid, according as enolisation gives rise to type (i) or (ii); actually, the latter substances are produced, and although the absence of enolisation to type (i) is not definitely excluded, it appears certain that at least 95% of the transformed substance belongs to type (ii). It is, however, remarkable that about 60% of the original material remains unaffected by ozone, although titration by Meyer's method indicates the presence of more than 90% of enol. The products obtained from 1 : 3-diketo-2-benzoylhydrindene are phthalic acid, a strongly reducing substance, which is probably phenylglyoxal, benzoic acid, and carbon dioxide; triketohydrindene cannot be detected, and is probably destroyed by oxidation. Only about 80% of the original substance enters into action, although the Meyer titration method indicates an almost exclusively enolic form. It appears that about 40% of the enolised portion belongs to type (ii).   H. W.

Some Properties of Benzanthrone. ARTHUR GEORGE PERKIN (T., 1920, **117**, 696—708).

4-Chloro-1-hydroxyanthraquinone. FRITZ ULLMANN and ACHILLE CONZETTI (*Ber.*, 1920, **53**, [*B*], 826—837).—1-Hydroxyanthraquinone is conveniently prepared by the diazotisation of a solution of 1-aminoanthraquinone in concentrated sulphuric acid, and is transformed by sulphuryl chloride in the presence of nitrobenzene at 100° into 4-*chloro*-1-*hydroxyanthraquinone*, which, when obtained in this manner, can only be freed with difficulty from small amounts of dichlorohydroxyanthraquinone; if the chlorination is effected in the presence of a little iodine, 2 : 4-*dichloro*-1-*hydroxyanthraquinone*, shining, yellow needles, m. p. 242°, is obtained. The constitution of the substances is deduced from their synthesis in the following manner : (i) phthalic anhydride is condensed with *p*-chlorophenol in acetylene tetrachloride solution in the presence of aluminium chloride to 5-*chloro*-2-*hydroxy-o-benzoyl-benzoic acid*, HO·C₆H₃Cl·CO·C₆H₄·CO₂H, colourless leaflets, m. p. 202° after softening slightly at 196°, which is transformed by sulphuric acid monohydrate into 4-chloro-1-hydroxyanthraquinone, small, yellow crystals, m. p. 193° (corr.); (ii) a molten mixture of phthalic anhydride and 2 : 4-dichlorophenol is converted by aluminium chloride into 3 : 5-*dichloro*-2-*hydroxy-o-benzoylbenzoic acid*, colourless leaflets, m. p. 204° (corr.), which is then transformed into 2 : 4-dichloro-1-hydroxyanthraquinone, m. p. 242°, in the usual manner. 4-Chloro-1-hydroxyanthraquinone is readily converted into 1 : 4-dichloroanthraquinone, m. p. 187°, by phosphorus pentachloride at 155—160° if care is taken to remove the phosphoryl chloride as rapidly as it is formed; under similar conditions, 2 : 4-dichloro-1-hydroxyanthraquinone gives 1 : 2 : 4-trichloroanthraquinone, m. p. 185·5° (corr.). The α-chloro-atoms of the hydroxyanthraquinones may be replaced by the hydroxyl group by treatment with boric and sulphuric acids at 156—160°, thereby yielding

1:4-*dihydroxyanthraquinone*, m. p. 198° (corr.), and 2-chloro-1:4-dihydroxyanthraquinone, dark red, shining needles, m. p. 239°, respectively. 4-Chloro-1-hydroxyanthraquinone is transformed by *p*-toluenesulphonamide in amyl-alcoholic solution in the presence of copper and potassium acetates into 1-*hydroxy*-4-p-*toluenesulphonamidoanthraquinone*, orange-yellow needles, m. p. 197°, which is hydrolysed by concentrated sulphuric acid to 4-amino-1-hydroxyanthraquinone, dark red, metallic needles, m. p. 215° (Wacker, A., 1903, i, 132, gives 207—208°). 2-*Chloro*-1-*hydroxy*-4-p-*toluenesulphonamidoanthraquinone*, pale red needles, m. p. 198°, and 2-*chloro*-4-*amino*-1-*hydroxyanthraquinone*, wine-red needles, m. p. 236°, are similarly derived from 2:4-dichloro-1-hydroxyanthraquinone. 1-*Hydroxy*-4-*anilinoanthraquinone*, dark violet, shining leaflets, m. p. 161°, is obtained from the monochloroanthraquinone, aniline, potassium acetate, and a trace of copper acetate. The similarly prepared 2 - *chloro* - 1 - *hydroxy* - 4 - *anilinoanthraquinone* crystallises in dark violet needles, m. p. 195°. N[1-*Hydroxyanthraquinonyl*-4]-*anthranilic acid* is most conveniently prepared by boiling a solution of 4-chloro-1-hydroxyanthraquinone and anthranilic acid in amyl alcohol with anhydrous potassium acetate in the presence of copper acetate and copper
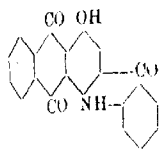
powder; it forms bluish-violet, shining needles, m. p. 272° (corr.; decomp.). The substance is not transformed into 4-*hydroxyanthraquinone*-2 : 1-*acridone* (annexed formula) by sulphuric acid or phosphoric oxide, but the conversion may be effected by the action of acetic anhydride in the presence of pyridine, and subsequent treatment of the acetyl *derivative* so formed with *p*-toluenesulphonyl chloride; the acridone crystallises in shining, blue leaflets, m. p. 321°, and gives blue shades on cotton from a wine-red vat.

H. W.

Condensations at Double Bonds. I. Condensation of Isoprene with *p*-Benzoquinone. H. von Euler and K. O. Josephson (*Ber.*, 1920, **53**, [B], 822—826). When isoprene is heated with one-sixth to one-seventh of its weight of *p*-benzoquinone for five to six hours at temperatures ranging from 120° to 180°,
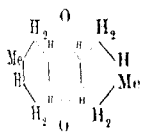
it readily yields a *product*, m. p. 234°, to which the annexed formula is assigned (in which the 2:7-position of the two methyl groups is uncertain). The mechanism of the reaction is therefore closely analogous to that of the condensation of isoprene to dimethyl*cyclo*octadiene. The substance readily unites with bromine in glacial acetic acid solution, yielding the *tetrabromide*, $C_{16}H_{20}O_2Br_4$, m. p. 210° (corr.; decomp.). With hydroxylamine, it gives a *dioxime*, which commences to decompose above 200°, and probably also a *monoxime*. Preliminary experiments show that it is readily oxidised by per-

manganate, and thereby undergoes very extensive decomposition. Reduction by hydrogen in ethereal solution in the presence of platinum-black appears to lead to the formation of a substance, $C_{16}H_{26}O_2$. H. W.

The Camphane Series. XXXVIII. The Cyanohydrazone of Camphorquinone. MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (T., 1920, **117**, 753—761).

Pulegonesulphonic Acid. The Behaviour of Sabinol and Sabinene towards Sulphurous Acid and Thujone. OTTO WALLACH [with G. REGGELIN, F. RIESENER, and HEUBNER] (*Nachr. Ges. Wiss. Göttingen*, 1919, 321—336; from *Chem. Zentr.*, 1920, i, 671—672).—Pulegonesulphonic acid is obtained as an almost colourless syrup when an alcoholic solution of pulegone is saturated with sulphur dioxide and preserved in a closed vessel for several days at 20°; it forms well-crystallised salts, which obstinately retain water (the *magnesium, zinc, lead, barium, calcium, ammonium,* and *piperidine* compounds are described). Such of them as do not contain poisonous metals are devoid of physiological activity.

Purified sabinol is similarly converted into its *sulphonic acid* at 0°. (In addition, small quantities of an insoluble, amorphous *substance*, m. p. 213—215°, which appears to be an ester, and of a neutral *compound*, woolly needles, m. p. 147—148°, are obtained.) The acid has m. p. 98—99°, becomes discoloured, and finally liquefies on exposure to air; it behaves like an unsaturated substance towards bromine or potassium permanganate. Its constitution has not been definitely elucidated, but its conversion by potassium hydroxide solution (1:1) into an alcohol. which, after reduction and oxidation, yields thujone, b. p. 199—200°, indicates the annexed formula. On the other hand, an acid of this constitution should yield α-thujoketonic acid when cautiously oxidised by potassium permanganate, but this product has not been obtained so far.

Me
SO$_3$H
C$_3$H$_7$
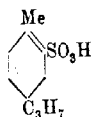
Sabinol is converted by hydrogenation in the presence of palladium chloride into a hydrocarbon, b. p. 161—163°, D²¹ 0·795. n_D 1·4375, and an alcohol, b. p. 206—208°, D²⁰ 0·9090, n_D 1·4576, the latter being the main product. It is oxidised by the calculated quantity of chromic acid in glacial acetic acid solution to *l*-thujone, b. p. 203—205°, D²⁰ 0·907, n_D 1·4507, $[\alpha]_D$ − 30·62° in 16·1% methyl-alcoholic solution. Potassium permanganate converts it into α-thujoketonic acid. The unusually high specific rotation indicates the possible presence of a third isomeride of thujone.

Oils containing thujone become strongly acidic when preserved, mainly owing to the formation of α-thujoketonic acid. H. W.

Homocamphor. ARTHUR LAPWORTH and FRANK ALBERT ROYLE (T., 1920, **117**, 743—750).

Preparation and Properties of *iso*Amylcamphor and Some of its Derivatives. FÉLIX MARTIN (*J. Pharm. Chim.,* 1920, [vii], **21**, 417—425).—A mixture of *iso*amylcamphor and *iso*amylcamphol is obtained by dissolving one atomic equivalent of sodium in an excess of *iso*amyl alcohol, adding one molecular equivalent of camphor, and heating the mixture at 140° for fifteen hours under a reflux apparatus.   The mixture of the two substances when oxidised with permanganate in benzene solution yields iso*amylcamphor*, a yellow, odourless oil, b. p. 165°/33 mm., D_4^{15} 0·9272, $[\alpha]_D^{18}$ + 59° (in alcohol), + 38·4° (in benzene).   Reduction with sodium in alcoholic solution converts the mixture into iso*amylcamphol*, m. p. 25—28°, b. p. 190°/61 mm., D_4^0 0·9611, $[\alpha]_D^{21}$ + 17° (in alcohol).   iso*Amylcamphyl acetate*, a colourless liquid, b. p. 169°/30 mm., D_4^{15} 0·9402, $[\alpha]_D^{18}$ + 7·24° (in alcohol), is obtained by acetylating *iso*amylcamphol.   W. P. S.

Tricyclene. P. LIPP (*Ber.,* 1920, **53**, [*B*], 769—781).—It has been suggested by Semmler that tricyclene is an intermediate product in the conversion of borneol or *iso*borneol into camphene. Since, however, the formulation of this substance has been doubted by Meerwein (A., 1914, i, 850), although the objections he raises have been partly removed by Ruziska (A., 1918, i, 398), the author has endeavoured to prepare the hydrocarbon from a similarly constituted substance, and for this purpose has chosen tricyclenic [dehydrocamphenylic] acid, the formula of which has been established with practical certainty by Komppa and Hintikka (A., 1908, i, 852), and by Komppa (A., 1911, i, 642).   He has thereby succeeded in establishing definitely the constitution of the hydrocarbon and in showing that it is readily converted by sodium hydrogen sulphate at 160° into camphene, but not by zinc chloride in benzene solution.   Tricyclene may therefore be an intermediate product in the formation of camphene from borneol, but not from *iso*borneol.

An ethereal solution of tricyclenyl chloride is converted by gaseous ammonia into tricyclenamide, shining, rhombic leaflets, m. p. 117—118° (corr.) (Komppa and Hintikka, *loc. cit.,* give 114·5°), which is transformed by phosphorus trichloride into *tricyclenylonitrile*, b. p. 100—102° (corr.) 12 mm., m. p. 65—70°.   The latter is reduced by sodium and alcohol to *ω-aminotricyclen*- (annexed formula), colourless, paraffin-like mass, which melts with the warmth of the hand and has b. p. *ca.* 100—101°/27 mm. (the *hydrochloride,* colourless leaflets which does not melt below 266°, and the *carbonate,* slender needles, m. p. 97—100° [slight decomp.], are described).   Attempts to convert the base into the corresponding primary alcohol by means of sodium nitrite and hydrochloric acid were unsuccessful, an oily, heterogeneous product being obtained, which owed its formation to rupture of the ring system.   The ease with which this occurs is
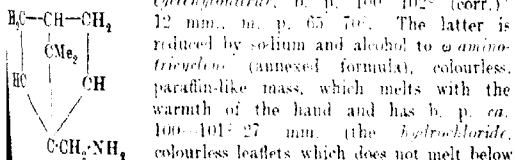
further illustrated by the conversion of ω-aminotricyclene hydro-
chloride into camphenilanaldehyde and ammonia by warming for a
short time with fuming hydrochloric acid.

A more successful series of experiments has tricyclenic acid for
its starting point. The latter is converted by methyl alcohol and
sulphuric acid into *methyl tricyclenate*, m. p. 38°, b. p. 99° (corr.)/
14 mm., D_i^{26} 1·0255, n_D^{26} 1·46953, which is reduced by sodium and
alcohol to *tricyclol*, colourless needles, m. p. 111—112° (corr.), b. p.
141°/71 mm. (*phenylurethane*, long, slender needles, m. p. 92—93°
[corr.]; *tricyclyl chloride*, b. p. 85—88°/14·5 mm., 81—82·5°/
11 mm.). The alcohol is converted by chromic acid in acetic acid
solution into *tricyclal*, b. p. 113—115°/31 mm., the smooth con-
version of which into tricyclenic acid shows that the carbon skeleton
has been unchanged up to this point (*tricyclalsemicarbazone*
forms small, matt needles, m. p. 219—220° [decomp.]). *Tricyclal-
azine*, prisms or cubes, m. p. 171—172° (corr.), is prepared by the
action of hydrazine hydrate on the aldehyde, and is converted by
an excess of hydrazine into the *monohydrazone*, which could not
be obtained in the pure condition; the crude product was there-
fore directly heated at 180—195° with a solution of sodium in
alcohol, whereby it was almost quantitatively transformed into
tricyclene, mixed, however, with small quantities of an unsaturated
hydrocarbon, probably camphene. The latter can be removed by
treatment with potassium permanganate in glacial acetic acid solu-
tion, thus yielding ultimately pure tricyclene, b. p. 151·6—152°
(corr.)/736 mm., m. p. 64—65°. The hydrocarbon is somewhat
readily affected by potassium permanganate in warm glacial acetic
acid solution, yielding tricyclenic acid and a carbonyl compound;
the formation of the former shows that the hydrazone fission has
occurred in the normal manner, and also that the same ring system
is common to tricyclene and tricyclenic acid.   H. W.

Croton Resin. R. BOEHM (*Arch. expt. Path. Pharm.*, 1915,
79, 138—154).—The optical activity of croton oil is due to a resin
which is dissolved in it. On removing the resin from the oil by
extraction with methyl alcohol, the oil becomes inactive. The
optical rotation of a croton oil may therefore serve as an indicator
of its resin content. This resin has already been described by
Dunstan and Boole (A., 1895, i, 680), but the author gives an
improved method for its extraction. Croton resin is a practically
colourless, light powder with no definite melting point. It becomes
soft, but not liquid, at 80—90°. It is sparingly soluble in water
and soluble in all proportions in organic solvents with the excep-
tion of light petroleums. The mean iodine value is 76·98. The
rotation of various samples ranged from $[a]_D + 49·96°$ to $+ 63·23°$.
Discordant results were obtained on analysis and molecular-
weight determinations of different samples; the formula $C_{36}H_{54}O_9$
and mol. wt. 627 are suggested with reservation. An attempt to
throw some light on the constitution of the compound failed. The
pharmacological activity of the resin is similar to that observed
previously with croton oil.   S. S. Z.

Synthesis and Constitution of Anemonin. Y. ASAHINA and A. FUJITA (*J. Pharm. Soc. Japan*, 1920, **455**, 1).—The chief results of this investigation may be summarised as follows: The sharp, oily substance volatile with steam obtained from *Ranunculus sceleratus* L., consists in the main of the parent substance of anemonin, and has been given the name *protoanemonin*, which under spontaneous union of 2 mols. passes into anemonin. The synthesis of protoanemonin (V) was effected in the following manner: Lævulic acid (I) is converted into β-bromolævulic acid (II), and the latter acetylated; the resulting acetyl derivative (III) in anhydrous ether is digested with anhydrous sodium acetate, the acetylacetoacrylic acid (IV) doubtless formed thereby yielding on distillation a strongly vesicant oil protoanemonin, which on stirring quickly changes into anemonin (VI), m. p. 158°. Anemonin

$$CH_2Ac \cdot CH_2 \cdot CO_2H \longrightarrow CHAcBr \cdot CH_2 \cdot CO_2H \longrightarrow$$

(I.) (II.)

(III.)

(IV.) (V.) (VI.)
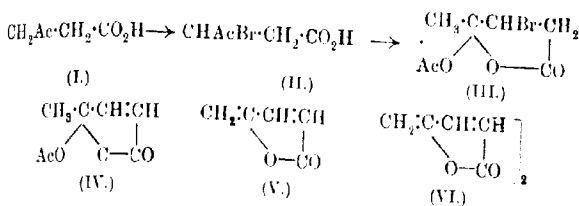
was also prepared, but in poorer yield, by similar treatment of dibromoangelicalactone. Owing to the unpleasant physiological action of ranunkel oil, an attempt was made to convert it into dihydroanemonin (IX). The latter could not be isolated in a pure condition, but was characterised by means of its semicarbazone, m. p. 185°, identical with the semicarbazone of lævulic acid, CH₂(CN·NH·CO·NH₂)·CH·CH₂·CO₂H. Anemonin is thus shown to be a dimeric product of protoanemonin and is constituted in accordance with the formula (VIII), whilst tetrahydroanemonin and dihydroanemonin have the constitutions represented by (VII) and (IX) respectively.

(VII.) (VIII.) (IX.)
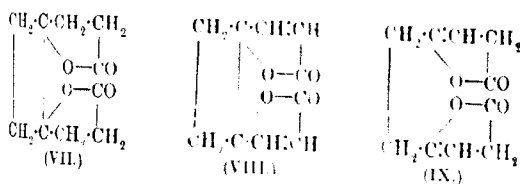
Colloid Chemical Studies on the Acids of Hop Bitters.
H. LÜERS and A. BAUMANN (*Kolloid Zeitsch.*, 1920, **26**, 202—212). —The properties of the acid of hop bitters, both in aqueous solution and in wort, have been investigated by means of the change in surface tension which this substance brings about. Humulon (α hop

bitter acid) exists in the form of an hydrosol as a typical colloid-disperse system with a negative charge and in character intermediate between a suspensoid and an emulsoid. It is coagulated by heavy metals and is further dispersed by salts of the alkali metals. The presence of anions changes the surface tension of the solutions in the order chlorion<thiocyanate ion<iodion<sulphion <tartration. The humulon hydrosol changes its dispersity spontaneously with time in the sense that the particles become larger with a simultaneous increase in the surface tension. In acid solutions, the surface tension is smallest, the bitter taste least pronounced and the turbidity greatest, whilst in alkaline solution the reverse is the case. Emulsions exercise a dispersing action on humulon hydrosol; this is particularly the case with gelatin, which differs from the other emulsoids in causing a large reduction of the surface tension of solutions of the humulon hydrosol. Hand in hand with the change in the dispersity, a very marked stabilising of the sol occurs. Humulon is strongly adsorbed by charcoal from aqueous solution, but less strongly from solutions of sodium potassium tartrate. With decreasing dispersion, the adsorption of humulon increases. The concentration of the sol and the surface tension of the solution follow a parabolic equation of the same form as the adsorption law. The power of humulon to form a stable foam is in keeping with its power of reducing surface tension and its adsorption. The changes which occur in humulon on boiling are considered in connexion with the processes occurring in brewing.   J. F. S.

Hyptolide, a Bitter Principle of Hyptis pectinata, Poit. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 327—337). —The leaves of this Labiate are extracted with 95% alcohol; an equal volume of water is added, and after filtering off the chlorophyll, the filtrate is concentrated until there crystallises *hyptolide*, $C_{18}H_{26}O_8$, colourless needles, m. p. 88·5°. $[a]_D^{27} +6·75°$. Yield, 2% of the leaves. The substance dissolves in 50 parts of boiling water and readily in most organic solvents; it distils unchanged under reduced pressure. It contains a lactone group (hence the name) and three acetyl groups. After oxidation with silver oxide in alkaline solution and hydrolysis, four equivalents of acetic acid are liberated. the fourth one resulting apparently from the oxidation of a terminal group $CH(OH)·CH_3$. This group is eliminated to some extent as acetone by steam distillation with 10% sodium hydroxide, when at the same time an additional carboxyl group is generated. The mechanism of this reaction is represented as follows, where the group R contains the preformed carboxyl of the lactone,

$$OH·CRR'·CH(OH)·CH(OH)·CHMe·OH \rightarrow$$
$$CRR':C(OH)·CH:CMe·OH \rightarrow CHRR'·CO·CH_2·COMe \rightarrow$$
$$CHRR'·CO_2H + COMe_2.$$
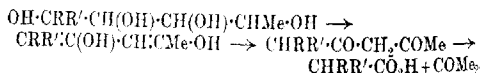
Reduction in alcoholic solution with hydrogen and palladium

chloride introduces six atoms of hydrogen, transforming the compound $C_{10}H_{14}Me(OAc)_3<^{CO}_{O}$ into an oil,

$$OH \cdot C_{10}H_{16}Me(OAc)_3 \cdot CH_2 \cdot OH.$$
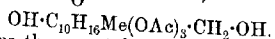
The latter contains three acetyl groups, but no lactone grouping; on boiling with acetic anhydride, one of the hydroxyl groups is eliminated as water, the other is acetylated; the resulting tetra-acetyl derivative is an oil.

Oxidation of hexahydrohyptolide with potassium permanganate in alkaline solution gives one-third of its weight as a mixture of acids; from water there first crystallises a dibasic *acid*, $C_9H_{16}O_4$, needles, m. p. 130—131°, soluble in 180 parts of water at 26°, dissociation constant, $4 \cdot 2 \times 10^{-5}$. The residue from the mother liquor of this acid was esterified, the ester was distilled, and after hydrolysis yielded $\alpha\alpha$-dimethylglutaric acid, $C_7H_{12}O_4$. Hence it is concluded that the acid $C_9H_{16}O_4$ must be either $\alpha\beta\beta$- or $\alpha\alpha'\alpha'$-trimethyladipic. The latter acid is known and melts at 115°, so that the acid from hexahydrohyptolide is considered to be identical with the former.

Oxidation of hexahydrohyptolide with nitric acid (D 1·2) on the water bath also yields a small quantity of this supposed $\alpha\beta\beta$-trimethyladipic acid, together with succinic acid. The following formula for the hexahydro derivative is arrived at:

$$OH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot CMe(OH) \cdot [CH(OAc)]_3 \cdot CH_3;$$
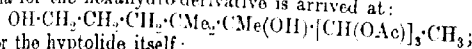
and for the hyptolide itself:

$$\begin{matrix} CH \cdot CMe_2 \\ \| \\ CH \cdot CO \cdot O \end{matrix} \Big> CMe \cdot [CH(OAc)]_3 \cdot CH_3 .$$
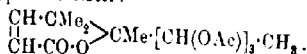
G. B.

Reduction of Elsholtzia Ketone [Elsholtzione]. MICHIZO ASANO (*J. Pharm. Soc. Japan*, 1919, **454**. 999—1006).—Elsholtzione, $CH_3Pr^\beta \cdot CO \cdot C \underset{O---CH}{\overset{CMe \cdot CH}{\diagup}}$ (A., 1915. i. 430), the reduction of which by the Clemensen and the Sabatier and Senderens methods has been unsuccessfully attempted by Asahina and his co-workers, is reduced by heating in a sealed tube with sodium ethoxide and hydrazine sulphate to *3-methyl-2-isoamylfuran*, b. p. 172° atm. or 78—79° 25 mm., D_4^{22} 0·8814, n_D^{23} 1·45178. This substance is not identical with dihydroperillen (b. p. 182°, D_4^{22} 0·8852, n_D^{22} 1·45762); consequently, the positions of the two substituents in perillen, $CH_2 \colon CMe \cdot CH_2 \cdot CH_2 \cdot C_5H_5MeO$), are still undetermined.

CHEMICAL ABSTRACTS.

8-Hydroxy-2 : 3-quinoxanthone. HARRY FITZGIBBON DEAN and MAXIMILIAN NIERENSTEIN (T., 1920, **117**. 802—806).

An Alkaloid in the Toxin of Bufo vulgaris. HANS HANDOVSKY (*Arch. Exp. Path. Pharm.*, 1920, **86**. 138—159).—The aqueous extract of the toxin from *Bufo vulgaris* after being freed from the colloid it contains was treated with chloroform in order to

remove the bufotalin, and was precipitated with phosphotungstic acid in the presence of sulphuric acid. The precipitate was again brought into solution by various methods which are described, and extracted with ether. Some anhydrous oxalic acid was then added to the dehydrated ethereal extract, when the new alkaloid, *bufo-tenine*, crystallised as its oxalate, $(C_6H_9ON)_2,C_2H_2O_4$. The author adduces evidence for the provisional constitution

$$\begin{array}{c} \text{CHMe·CO} \\ | \qquad\qquad\Big\rangle\text{NMe.} \\ \text{CH==CH} \end{array}$$
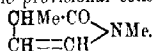
                                                                S. S. Z.

Cinchona Alkaloids. III. Nitro- and Amino-sulphonic Acids, Nitro- and Amino-bases of some Hydrogenated Cinchona Alkaloids. G. GIEMSA and J. HALBERKANN (*Ber.*, 1920, **53**, [*B*], 732—750. Compare A., 1919. i. 342).—The hydrogenated alkaloids under investigation are smoothly converted by concentrated sulphuric acid and the calculated quantity of nitric acid (D 1·4) or nitrate into crystalline nitro-sulphonic acids, which are easily hydrolysed by warm 25% hydrochloric acid, and thus particularly adapted to the preparations of the pure nitro-bases. They are readily reduced to the corresponding amino-sulphonic acids by ferrous sulphate in the presence of alkali, and this behaviour is of the greater importance, since the amino-bases are not readily sulphonated. The amines themselves are smoothly obtained by hydrolysis of the aminosulphonic acids. The introduction of the nitro-group is found to increase the negative specific rotation of the compounds, whilst the amino-group displaces the rotation in the dextro-direction; the latter tendency is strengthened by the introduction of the sulphonic radicle to such an extent that amino-hydroquininesulphonic acid is dextrorotatory.

The following individual compounds are described : 5-*Nitrohydro-cupreinesulphonic acid*, $C_{19}H_{23}O_7N_3S$, coarse, golden-yellow prisms, which gradually become green on exposure to sunlight and darken at 205°, and completely decompose, without melting, above 245°. 5-*Nitrohydroquininesulphonic acid*, anhydrous, yellow needles, which are sensitive to light and decompose above about 230°, $[\alpha]_\text{D}^{20} -172\cdot4°$ (in alcohol), $-186\cdot7°$ (in alcohol and 10% aqueous ammonia). 5-*Nitroethylhydrocupreinesulphonic acid*, yellow, prismatic needles, sensitive to light and decomposing above about 270°. *Nitrohydrocinchoninesulphonic acid*, yellow, microscopic platelets or cubes or prismatic rods ($+H_2O$), thin, rectangular plates ($+2H_2O$), m. p. (anhydrous) 236° (decomp.). *Nitrohydro-cinchonidinesulphonic acid*, pale yellow, four-sided platelets, decomposing above *ca.* 270°. *Nitrohydrocupreine*, $C_{19}H_{23}O_4N_3$ (from the sulphonic acid and hydrochloric acid [D 1·126]), coarse, red crystals, m. p. 192° (decomp.) after darkening at about 180°. 5-*Nitrohydro-quinine*, pale yellow, anhydrous crystals, which are alkaline towards litmus, m. p. 210—212° (decomp.) (the *monosulphate*, golden-yellow prisms [$+15H_2O$] and the *disulphate*, yellow, amorphous powder [$+2H_2O$], are described). 5-*Nitroethylhydrocupreine*, almost colourless, anhydrous leaflets, m. p. 221—223° (decomp.), $[\alpha]_\text{D}^{20} -256\cdot4°$ in alcohol, $-222\cdot1°$ in chloroform. *Nitrohydro-*

-inchonine, coarse, pale, yellow, anhydrous plates, m. p. 234—235°
(decomp.), $[\alpha]_D^{20} + 163°$ in alcohol, $+161\cdot8°$ in chloroform. *Nitro-hydrocinchonidine*, yellow, crystalline powder, m. p. 148°
(decomp.), $[\alpha]_D^{20} - 65\cdot2°$ in alcohol, $-60\cdot4°$ in chloroform.
5-Aminohydroquininesulphonic acid, yellow, anhydrous needles,
m. p. about 227° (decomp.) after darkening at about 218°,
or coarse, yellow prisms $(+3H_2O)$, $[\alpha]_D^{20} + 18\cdot85°$ in absolute
alcohol, $+15\cdot8°$ in a mixture of alcohol and aqueous ammonia (the
monosulphate, reddish-brown needles $[+3H_2O]$ or yellowish-red,
amorphous powder $[+H_2O]$, is described). *5-Aminoethylhydro-cupreinesulphonic acid*, pale yellow needles $(+H_2O)$, which become
anhydrous and intensely reddish-brown when preserved over
sulphuric acid. *Aminohydrocinchoninesulphonic acid*, almost colour-
less, coarse, anhydrous needles, m. p. 276° (decomp.). *Aminohydro-inchonidinesulphonic acid*, practically colourless, anhydrous
needles. m. p. 282° (decomp.). 5-Aminohydroquinine (by hydrolysis
of the aminosulphonic acid or reduction of the corresponding nitro-
derivative by ferrous sulphate), yellow needles, m. p. 216—218°,
$\alpha_D^{20} - 19\cdot99°$ in absolute alcohol, $-120\cdot9°$ in ether (the *sulphate*,
yellowish-red crystals $[+5H_2O]$, is described). 5-Aminoethylhydro-
cupreine, from the aminosulphonic acid or the corresponding nitro-
compound. m. p. 212°, $[\alpha]_D^{20} - 16\cdot98°$ in alcohol, $-123\cdot8°$ in ether.
identical with the base prepared previously (*loc. cit.*) from the
azo-compound. *Aminohydrocinchonine*, yellow, prismatic plates or
colourless needles, according to the solvent used for crystallisation,
m. p. 217°, $[\alpha]_D^{20} + 204°$ in absolute alcohol. *Aminohydro-cinchonidine*, colourless needles, m. p. 170°, to a yellow liquid,
$\alpha_D^{25} - 80\cdot7°$ in absolute alcohol.

H. W.

Hygrine Alkaloids. III. Constitution of Cuskhygrine. Conversion of Cuskhygrine into Hygrine. KURT HESS and

HEINRICH FINK (*Ber.*, 1920, **53**, [*B*], 781—809. Compare A.,
1913. i. 1378; 1914, i. 1991. Cuskhygrine has been isolated by
Liebermann from the liquid mixture
of bases obtained in the preparation
of cocaine, and on account of its
empirical composition and its oxida-
tion to hygric acid (1-methyl-
pyrrolidine-2-carboxylic acid) has been assigned the annexed
formula, in which, however, the symmetrical arrangement and the
presence of the second pyrrolidine ring cannot be regarded as
proved. The authors now bring definite evidence to show the
presence of the carbonyl group, but find that cuskhygrine does not
condense with benzaldehyde, oxalic ester, or amyl nitrite, and
hence does not contain the active methylene group which the
above formula indicates. Further examination leads them to
assign the constitution shown by the
annexed formula to the base, the most
important evidence for which is founded
on the observations of Traube on the
action of nitric oxide on ketones in the
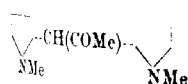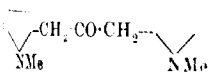
presence of sodium ethoxide. Under these conditions, one mole-cule of cuskhygrine invariably absorbs six molecules of the gas. The primary additive product was too unstable to permit its isola-tion, but, on hydrolysis, yielded the sodium compound of methylene-diisonitroamine, $CH_2(N_2O_2Na)_2$; the latter can only result from the presence of a methyl group, and accounts for the absorption of four molecules of nitric oxide. Since, according to Traube, a methylene group reacts more readily than the methyl radicle, it follows that such a group cannot be present in cuskhygrine, and that the absorption of the two remaining molecules of the gas is due to the presence of a methine group. Further products of the fission of cuskhygrine *iso*nitroamine are 1-methyl-2-pyrrolidylacetic acid and a non-homogeneous, basic oil, which, after hydrogenation and treatment with sodium methoxide and methyl iodide, gives a uniform biquaternary iodide (annexed formula), thus affording convincing proof of the presence of a second pyrrolidine ring. Additional evidence in favour of the newer formula is also provided by the isolation of two isomeric hydrazones, which is impossible if the constitution assigned by Liebermann be accepted.
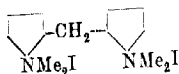
Cuskhygrine, b. p. 169—170°/23 mm., is converted by hydroxyl-amine into the corresponding *oxime*, flat pyramids, m. p. 53—54°, which does not undergo the Beckmann transformation when treated with phosphorus pentachloride, glacial acetic-hydrochloric acids, or sulphuric acid. The *semicarbazone* is a non-crystalline syrup. *Cuskhygrine-α-hydrazone*, colourless, syrupy oil, which has a marked tendency towards polymerisation, b. p. 182—183°/14 mm., is obtained in quantitative yield by the action of hydrazine hydrate on an alcoholic solution of the base; in addition to this substance, *cuskhygrine-β-hydrazone*, b. p. 119—120°/15 mm., was obtained when (and only when) an old and somewhat decomposed specimen of hydrazine hydrate was used. The α-hydrazone is only converted by sodium ethoxide to a relatively small extent into the corre-sponding *amine*, b. p. *ca.* 125°/16 mm., which gives a *picrate*, long needles, m. p. 185°; the β-hydrazone, on the other hand, yielded a *product*, b. p. 95—99°/20 mm., the *picrate* of which was found to be identical with that of di-1-methyl-2-pyrrolidylmethane (see later).

The products of the action of nitric oxide on cuskhygrine, and subsequent hydrolysis of the primary compound, were isolated in the following manner: (i) Methylenedi*iso*nitroamine was identified as the crystalline barium salt, $CH_2O_4N_4Ba.3H_2O$, which was further characterised by conversion into the silver salt and the dimethyl ester, m. p. 134°. (ii) 1-Methyl-2-pyrrolidylacetic acid was con-verted into its *ethyl* ester, colourless oil with basic, aromatic odour, b. p. 89—90°/15 mm. (*picrate*, prisms, m. p. 113°; *methiodide*, coarse, prismatic needles, m. p. 105—106° after slight previous softening), and the latter was hydrolysed by aqueous barium hydr-oxide to 1-*methyl-2-pyrrolidylacetic acid*, colourless crystals, which are very susceptible to the action of air, m. p. 95° (the m. p. is

given with reserve, as a suitable solvent for recrystallisation of the acid has not been found). (iii) The basic constituents were separated into two fractions, of which that of higher b. p. consisted of unchanged cuskhygrine, whilst that of b. p. 90—98°/ 16 mm. was found to be composed of a mixture of bases, which could not be separated by distillation. It did not yield a crystalline picrate, and was therefore hydrogenated in the presence of colloidal platinum. The mixture of saturated bases, b. p. 99—109°/16 mm., yielded a picrate, which gradually became completely solid, and, after repeated crystallisation, gave a pure specimen of di-1-methyl-2-pyrrolidylmethane picrate, m. p. 203° (see above). The action of formaldehyde and formic acid on the hydrogenated bases (which thus consist of a mixture of partly demethylated and methylated di-1-methyl-2-pyrrolidylmethanes) did not give a homogeneous product, but a more successful result was obtained by exhaustive methylation with sodium methoxide and methyl iodide, whereby the 1:1'-*dimethiodide* of *di-1-methyl-2-pyrrolidylmethane* was prepared in cubic crystals. m. p. 200° after slight previous softening; it was further characterised by converting it, by means of silver chloride, into the *methochloride*, and transformation of the latter into the *aurichloride*, canary-yellow, microcrystalline powder, which decomposed at 260°.

When an ethereal solution of cuskhygrine is allowed to remain for a considerable time in contact with solid potassium hydroxide, the base undergoes a partial conversion into *ψ*-hygrine (the picrate of the latter has m. p. 149 150°, instead of 174° [corr.], after softening at 160°, as previously recorded), brown, viscous products being simultaneously formed. A similar change is observed when cuskhygrine is boiled for some time with aqueous-alcoholic potassium hydroxide solution.   H. W.

Pelletierine and Methylpelletierine. GEORGES TANRET (*Compt. rend.*, 1920, **170**, 1118 1120). The author reaffirms his results as to the properties of the two alkaloids, pelletierine and methylpelletierine, found in the bark of the pomegranate tree (compare A., 1880, 481), and refutes the statements of Hess and Eichel (compare A., 1917, i, 349; 1918, i, 33, 34) as to the non-existence of optically active forms of these alkaloids. Certain salts are described.

Pelletierine, $[\alpha]_D$ −31·1°, gives a *sulphate*, m. p. 133°, $[\alpha]_D$ −30·3°; a *hydrochloride*, m. p. 145°, $[\alpha]_D$ −41·2°; a *hydrobromide*, m. p. 137°, $[\alpha]_D$ −32·5°; a *nitrate*, m. p. 82 85°, $[\alpha]_D$ −34·8°; a *picrate*. m. p. 131 133°; a *platinichloride*, m. p. 214 216°; a *disulphotungstate*; an *acetyl* derivative, b. p. 205 210° 40 mm., $[\alpha]_D$ −32·6°; a *benzoyl* derivative, $[\alpha]_D$ −18·7°; and a *semicarbazone hydrochloride*, m. p. 168 170°, $[\alpha]_D$ −10·8°. Pelletierine is very sensitive to heat and to acids and bases, rapidly losing its optical activity.

Methylpelletierine, b. p. 106 108° 45 mm., $[\alpha]_D$ +27·7°, and in aqueous solution +24·1°, gives a *hydrochloride*, m. p. 168—170°,

$[a]_D + 41.2°$; a *hydrobromide*, m. p. 165—167°, $[a]_D + 33.5°$; a *sulphate*, $[a]_D + 38°$; a *picrate*, m. p. 157—159°; and a *platini-chloride*, m. p. 206—208°.   W. G.

The Chemical Isolation of **Vitamines.** C. N. MYERS and CARL VOEGTLIN (*J. Biol. Chem.*, 1920, **42**, 199—205).—Autolysed yeast filtrate is not a satisfactory product from which to attempt the isolation of the antineuritic vitamine. The active material is readily extracted from dried yeast by means of acidified methyl alcohol. From this fraction, an active, crystalline substance can be obtained by using Funk's silver acetate method, followed by mercuric sulphate precipitation. This substance becomes inactive on drying. The method eliminates purines, histidine, proteins, and albumoses. Stachydrine, trigonelline, and allied betaines show no antineuritic activity.   J. C. D.

Constitution of the Organic Nitrogen Bases of **Californian Petroleum.** C. F. MABERY and L. G. WESSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1011—1030).—A re-examination of the basic con-stituents of Californian petroleum (A., 1900, i, 533) has shown them to consist mainly of alkylated quinolines (or *iso*quinolines), with a small proportion of hydrogenated derivatives or pyridine compounds. By refractionation, the material was divided into fractions boiling over intervals of 2—4° covering a range of 130—283°/50—90 mm. The analysis and mol.-wt. determination of one of these agreed with the formula of an alkylated quinoline, $C_{15}H_{19}N$, whilst from another an acid ferrocyanide, derived from the base, $C_{13}H_{15}N$ was obtained. All the fractions yield pyridine pentacarboxylic acid and a methylpyridinetetracarboxylic acid when boiled with potassium permanganate solution, and therefore contain at least three alkyl groups, of which the relatively simple nature is shown by the absence of propionic, or higher fatty, acid from the oxidation products. 3-Methylquinoline was obtained by distilling with lime the chromic acid oxidation product of one fraction of base. A medium fraction yielded a phthalone derivative by condensation with phthalic anhydride. The bases are unchanged by nitrous acid, but can be reduced to secondary bases, from which nitroso-derivatives are obtainable. Thus, a product, b. p. 208—210°/90 mm., $C_{14}H_{20}N$ or $C_{14}H_{21}N$, was obtained from a fraction $C_{14}H_{17}N$. Unsuccessful attempts were made to break down the pyridine ring of the benzoylated reduction product by means of phosphorus pentachloride. Definite picrates, platini-chlorides, or double mercury salts could not be obtained from any fraction, probably because these, although representing a fairly satisfactory separation of the bases as regards molecular weight, are nevertheless mixtures containing small proportions of the other components previously mentioned. A lower fraction underwent sulphonation with fuming sulphuric acid, whilst a medium one was resistant to this agent. The action of bromine, iodine, hydriodic acid, and nitric acid is also described.   J. K.

A New Series of Nitrogenous Compounds obtained from Camphoroxalic Acid. PERCY CHORLEY and ARTHUR LAPWORTH (T., 1920, **117**, 728—742).

The Addition of 1 : 3-Diketones to Thiocarbimides. I. Acetylacetone and certain Aryl Thiocarbimides. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1055—1061).—Acetylacetone, in the form of its sodium salt, reacts at the ordinary temperature with thiocarbimides with formation of thioanilides. The acetyl group is removed from these compounds by solution in cold alkali hydroxide, and acidification at 0° after some hours. Both the resulting, and the original, thioanilides give the same products, and react very easily with phenylhydrazine and with hydroxylamine, phenylhydrazones and *iso*oxazoles being respectively produced, with elimination of the sulphur atom. *Thiodiacetoacetylanilide*, $CH_3 \cdot CO \cdot CH(CS \cdot NHPh) \cdot CO \cdot CH_3$, yellow needles, m. p. 107—108°, and *thioacetoacetylanilide*, $CH_3 \cdot CO \cdot CH_2 \cdot CS \cdot NHPh$, yellow plates, m. p. 63·5—64°, each give the phenylhydrazone of thioformanilide when treated with phenylhydrazine, and with

hydroxylamine, 3-*anilino*-5-*methyl*isoox*azole*, $O \diagdown \begin{matrix} CMe{:}CH \\ N{=}\!{=}C \cdot NHPh \end{matrix}$,

needles, m. p. 111—112°. *Thiodiacetoacetyl-p-toluidide*, $CHAc_2 \cdot CS \cdot NH \cdot C_6H_4Me$,

yellow plates. m. p. 132—133°; *thioacetoacetyl-p-toluidide*, $CH_2Ac \cdot CS \cdot NH \cdot C_6H_4Me$. yellow needles, m. p. 68—69°; 3-p-*tolu-*

idino-5-*methyl*isoox*azole*, $O \diagdown \begin{matrix} CMe{:}CH \\ N{=}\!{=}C \cdot NH \cdot C_6H_4Me \end{matrix}$, needles, m. p.

122—124°; *thiodiacetoacetyl-p-bromoanilide*,

$CHAc_2 \cdot CS \cdot NH \cdot C_6H_4Br$,

needles, m. p. 137—139°; *thioacetoacetyl-p-bromoanilide*,

$CH_2Ac \cdot CS \cdot NH \cdot C_6H_4Br$,

m. p. 110—111°; 3-p-*bromoanilino*-5-*methyl*isoox*azole*,

$O \diagdown \begin{matrix} CMe{:}CH \\ N{=}\!{=}C \cdot NH \cdot C_6H_4Br \end{matrix}$,

needles, m. p. 178—180°; *thiodiacetoacetyl-m-toluidide*, yellow plates, m. p. 124—125°; *thiodiacetoacetyl-o-toluidide*, yellow plates, m. p. 126·5—128°.

J. K.

Preparation of an Arylcarbamide Chloride. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 315237; additional to D.R.-P. 241822; from *Chem. Zentr.*, 1920, ii. 691).—p-Nitroaniline (in place of β-aminoanthraquinone) is treated with carbonyl chloride until the amine hydrochloride has completely disappeared with the object of preparing p-nitrophenylcarbamide chloride [p-*nitrophenylcarbamyl chloride*]; the temperature is below that at which the latter is converted into the corresponding carbimide. When carbonyl chloride is passed into a cooled suspension of p-nitroaniline in toluene, a mixture of p-nitrophenylcarbamyl chloride and nitroaniline hydrochloride is first produced; at the ordinary or slightly higher temperature, the latter is converted into

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the carbamyl chloride, hydrogen chloride being evolved. The pure substance is a valuable intermediate product in the preparation of carbamide derivatives, and, for example, is quantitatively transformed by a solution of aniline in benzene into *p*-nitrodiphenylcarbamide.   H. W.

Removal of Sulphur from Organic Compounds by means of Arsenic Trioxide. WALTHER HERZOG (*Zeitsch. angew. Chem.*, 1920, **33**, I, 140).—Organic compounds containing sulphur may be readily desulphurised by treatment with arsenic trioxide. The method is particularly suitable for the preparation of carbodiphenylimide from symmetrical diphenylthiocarbamide, which for the purpose is dissolved in xylene or other inert solvent and boiled with arsenic trioxide under reflux.   C. A. M.

Orientation of the Nitro- and Arylazo-glyoxalines. Fission of the Glyoxalone Nucleus. ROBERT GEORGE FARGHER (T., 1920, **117**, 668—680).

Action of Hydrazine on the Acyclic 1 : 4-Diketones. E. E. BLAISE (*Compt. rend.*, 1920, **170**, 1324—1326).—Hydrazine acts on acetonylacetone in hydrochloric acid solution to give a compound, $C_{12}H_{20}N_4$, m. p. 52—53°, which is probably a dimeride of the dihydropyridazine expected.

In acetic acid solution hydrazine gives with *s*-dipropionylethane, *diethyltetrahydropyridazine* (I), b. p. 100°/15 mm., giving a *benzoyl* derivative, b. p. 210°/16 mm., and *diethylpyridazine* (II),

(I.) CH₂〈 CH₂ CEt 〉N (II.) CH〈 CH CEt 〉N
      CHEt NH   CEt N
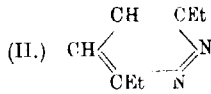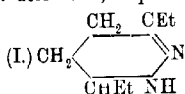
b. p. 121—122°/15 mm., giving a *platinichloride*, m. p. 180—182°, and a *picrate*, m. p. 108—109°.   W. G.

New Type of Di*iso*nitroso-peroxides. E. J. VIRGIN (*Diss. Upsala*, 1914, pp. 63).—1 : 2 : 4 : 5-*Tetraketo*-3 : 6-*dibenzoyl*-4 :5-*dihydropyridazine* [4 : 5-*diketo*-3 : 6-*dibenzoyl*-4 : 5-*dihydropyridazine* 1 : 2-*dioxide*] (A), $\begin{smallmatrix} NO:CBz\cdot CO \\ NO:CBz\cdot CO' \end{smallmatrix}$ red crystals exploding at 105—110° in a capillary tube, is obtained by warming αγδζ-tetraketo-αζ-diphenylhexane with nitrogen peroxide and ether at 25—27° for twenty minutes; it does not respond to the Liebermann nitrosoreaction. The mother liquors contain a small quantity of the substance O (see below). 1 : 5-*Dihydroxy*-2 : 4-*diketo*-3 : 6-*dibenzoyl*-1 : 4-*dihydropyridazine* [1 : 5-*dihydroxy*-4-*keto*-3 : 6-*dibenzoyl*-1 : 4-*dihydropyridazine* 2-*oxide*] (B), obtained from A by reduction in cold acetone with hydriodic acid (4 mols.) and a saturated solution of sulphur dioxide or with saturated hydrobromic acid, separates from acetone in pale yellow needles, m. p. 128° (decomp.), forms a *disodium* salt, develops a deep red coloration with ferric chloride in acetone solution, yields a *diacetyl* derivative, yellow needles, m. p. 160° (decomp.), and is reconverted into A by bromine

or nitrogen peroxide in ether or chloroform or by nitrous acid in ether. 1:5-*Dihydroxy-4-keto-3:6-dibenzoyl-1:4-dihydropyridazine* (C), obtained by keeping B with ice-cold acetic acid saturated with hydrogen iodide for two hours at the ordinary temperature and then adding a saturated solution of sulphur dioxide, separates from alcohol in anhydrous, yellow crystals, m. p. 181—182°, or as a *hydrate*, yellow, microscopic needles and prisms, decomp. 125°; with ferric chloride in alcohol and acetone it develops an intense red coloration, which changes through green to violet by the addition of water. ε-*Chloro-β-oximino-αγδζ-tetraketo-αζ-diphenylhexane* (D), obtained by treating an acetone solution of A with concentrated hydrochloric acid, crystallises from a mixture of ether and benzene in rhombic plates containing 1 mol. C_6H_6, develops a coloration with ferric chloride, and forms a *diacetyl* derivative, prisms, m. p. 156—157°. 3-*Chloro-1:5-dihydroxy-4-keto-6-benzoyl-1:4-dihydropyridazine* (E), obtained together with its isomeride F (below) by saturating a solution of B in 80% alcohol with hydrogen chloride at 0° and adding ether after concentration, forms yellow blades, m. p. 190° (decomp.). 6-*Chloro-1:5-dihydroxy-4-keto-3-benzoyl:4-dihydropyridazine* (F) separates from the alcoholic mother liquor in yellow crystals, m. p. 180°. 1:5-*Dihydroxy-4-keto-6-benzoyl-1:4-dihydropyridazine* (G), obtained by treating E with hydriodic acid, forms yellowish-brown plates, m. p. 245° (decomp.). 4:5-*Dihydroxy-6-benzoylpyridazine* (H), yellowish-white crystals, m. p. 239—240° (slight decomp.), is obtained from G in a similar manner. 1:5-*Dihydroxy-4-keto-6-benzyl-1:4-dihydropyridazine* (I), needles, m. p. 261° (decomp.), is obtained by warming G with a solution of hydrogen iodide in acetic acid; the mother liquor, after being neutralised, yields 4:5-*dihydroxy-6-benzylpyridazine* (J), m. p. 252—253° (decomp.), which can also be prepared from H, I, and K.

3-*Chloro-4:5-dihydroxy-6-benzoylpyridazine* (K), rectangular plates, m. p. 232—233°, is obtained by treating F for thirty minutes with an acetic acid solution of hydrogen iodide. 4:5-*Dihydroxy-6-benzoyl-3-benzylpyridazine* (L), pale yellow, rectangular prisms, m. p. 229—230° (*monoacetyl* derivative, yellow prisms, m. p. 189—190°), is obtained by boiling C with the same reagent. By heating C with this reagent in a sealed tube for five hours, 4:5-*dihydroxy-3:6-dibenzylpyridazine* (M), plates, m. p. above 300° (*monoacetyl* derivative, plates, m. p. 215°; *diacetyl* derivative, prisms, m. p. 147°), is obtained. βε-*Dioximino-αγδζ-tetraketo-αζ-diphenylhexane* (N), obtained by boiling B with acetone, forms thin prisms, m. p. 126° (decomp.), yields *oximinobenzoylacetic acid*, $CO_2H·CBz:NOH$, irregular prisms, m. p. 130° (decomp.), by treatment with sulphuric acid and acetone, and is converted into A and a small quantity of O by treatment with nitrogen peroxide in ethereal solution; it forms a *diacetyl* derivative, yellow crystals, m. p. 166°. By treatment with hydrogen chloride in acetic acid N is converted into an *isomeride* (O), the *diacetyl* derivative of which has m. p. 186—187°.

3:5-*Dibenzoyl*-1:2:4-*oxadiazole*, $CBz\!\!<^{N\cdot O}_{N\cdot CBz'}$ six-sided plates,

m. p. 105°, obtained by keeping A in methyl-alcoholic solution for twenty-four hours, forms a *diphenylhydrazone*, yellow needles, m. p. 171—172°. *Ethyl* 1:2:4:5-*tetraketo*-4:5-*dihydropyridazine*-3:6-*dicarboxylate* [*ethyl* 4:5-*diketo*-4:5-*dihydropyridazine*-3:6-*dicarboxylate* 1:2-*dioxide*], m. p. 70°, is obtained from ethyl ketipinate and nitrogen peroxide in ethereal solution at −15°.

The dioximino-peroxides of ethyl acetonedicarboxylate are discussed, and reasons for some types of its reactions are given, based on the behaviour of analogous compounds of A.

<div align="right">CHEMICAL ABSTRACTS.</div>

Bistetrazole. E. OLIVERI-MANDALÀ (*Gazzetta*, 1920, 50, i, 256—261. Compare A., 1913, i, 1398).—Bistetrazole exhibits great stability, and only by means of hot concentrated sulphuric acid or fused potassium hydroxide is its molecule profoundly decomposed. When treated with diazomethane in absolute ethereal solution, it yields, together with a small proportion of the dimethyl derivative, a compound which is isomeric with bistetrazole, but, unlike the latter, exhibits no acid characters; for this compound the structure $^{N\colon N}_{N\colon N}\!\!>CH\cdot CH\!\!<^{N\colon N}_{N\cdot N}$ is tentatively proposed.

Whereas concentrated sulphuric acid exerts oxidising and hydrolysing actions on bistetrazole, thus: $C_2H_2N_8 + 2H_2O + O = 3N_2 + 2CO_2 + 2NH_3$, fused potassium hydroxide decomposes it with formation of potassium azide, apparently in accordance with the equation $C_2H_2N_8 \longrightarrow 2N_3H + C_2N_2$. This tendency to lose azoimide, manifested generally by cyclic compounds containing the grouping ·N:N·NH·, is exhibited also by most compounds in which the triazo-group, $\cdot N\!\!<^{N}_{N}\!\!\rvert$, occurs; only azides of the following structures undergo decomposition with elimination of a molecule of nitrogen: (1) ·CO·CH·N$_3$ ⟶ N$_2$ + ·CO·C:NH, and (2) :CH·CO·N$_3$ ⟶ N$_2$ + :CH·CO·N: ⟶ :CH·N:CO.

The cryoscopic behaviour of bistetrazole in aqueous solution confirms the marked ionisation of this compound indicated by conductivity measurements (*loc. cit.*). In freezing acetic acid the molecular weight is normal.

The *isomeride* of bistetrazole (see above) forms acicular aggregates of crystals, m. p. 98—99°, and is insoluble in alkali carbonate solution.

Dimethylbistetrazole, $C_2N_8Me_2$, forms crystals, m. p. 150—160°, and yields nitrogen and methylamine when treated with concentrated alcoholic potassium hydroxide. The *sodium*, $C_2N_8Na_2$, *silver*, $C_2N_8Ag_2$, *barium*, $C_2N_8Ba,3H_2O$, and *copper*, C_2N_8Cu, salts were prepared and analysed; the copper and mercury salts explode violently when heated.   **T. H. P.**

The Structure and Properties of the Compound obtained by the Thermal Decomposition of *o*-**Methoxyphenyl Benzylidenehydrazinocarboxylate.** OTTO DIELS and HEINRICH GRUBE (*Ber.*, 1920, **53**, [*B*], 854—863).— In a previous communication (A., 1914, i, 940) it has been shown that *o*-methoxyphenyl benzylidenehydrazinocarboxylate is smoothly decomposed, when heated, into guaiacol and a sparingly soluble, crystalline substance, $(C_8H_6ON_2)_x$; the constitution of the latter is now shown to be represented by the formula $CHPh{:}N{\cdot}N{<}^{CO}_{CO}{>}N{\cdot}N{:}CHPh$.

The compound is decomposed by protracted heating with a mixture of glacial acetic and fuming hydrochloric acids into benzylideneurazine, $CHPh{:}N{\cdot}N{<}^{CO{\cdot}NH}_{CO{\cdot}NH}$, long, colourless needles, m. p. 254°, which is further decomposed by water into benzaldehyde and urazine. m. p. 270°. These reactions, however, throw but little light on the constitution of the substance, since the products could be equally well derived from a di- or tri-polymeride, discrimination between which cannot be effected by determination of the molecular weight on account of the very slight solubility of the substance. More information is afforded by its milder fission by means of phenylhydrazine in the presence of dimethylaniline, which gives rise to the *compound*, $CHPh{:}N{\cdot}N{<}^{CO}_{CO}{>}N{\cdot}NH_2$, colourless, crystalline powder, m. p. 254—255°, and phenyl enzylidenehydrazine. The presence of a free amino-group in the former is shown by its conversion into a *monoformyl* derivative, shining crystals, m. p. 78°, and a *diacetyl* compound, colourless, pearly leaflets, m. p. 169°, as well as by its condensation with furfuraldehyde and anisaldehyde with the formation of *derivatives*, $C_{15}H_{12}O_3N_4$, pale brown prisms, which decompose without melting at 251° after darkening at 247°, and $C_{17}H_{14}O_3N_4$, colourless crystals, m. p. 272—273°, to a reddish-brown liquid after becoming yellow at 268°. The close relationship of the amine to the parent substance is shown by its re-conversion into the latter when boiled with benzaldehyde in dimethylaniline solution in an atmosphere of carbon dioxide. The amine or its formyl derivative is converted by boiling aqueous potassium hydroxide solution into dibenzylidenecarbohydrazide, $CHPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh$, which when obtained in this manner forms small, canary-yellow leaflets, m. p. 138°; when, however, the compound is prepared by mixing alcoholic solutions of carbohydrazide and benzaldehyde in the usual manner, it is obtained in colourless leaflets. The same *formate*, colourless, silky, needles, m. p. 189—190°, with yellow coloration after softening at 187°, is obtained by the action of formic acid on either variety, and this is converted by alkali or by heat (with evolution of formic acid) into the yellow modification. Precisely similar observations with the *acetate* are recorded. Crystallographically, the modifications are identical with one another, and they also show the same

melting point since the colourless passes into the yellow variety when heated.   H. W.

Isomeric Phthalylhydrazides. FREDERICK DANIEL CHATTAWAY and WILLIAM TESH (T., 1920, **117**, 711—720).

Action of Benzyl Alcohol on Albumins and Ferments. J. JACOBSON (*Compt. rend. Soc. Biol.*, 1920, **83**, 255—256; from *Chem. Zentr.*, 1920, i, 783).—Benzyl alcohol precipitates egg-albumin and peptone even from solutions containing one part in a million, and the precipitates do not redissolve in distilled water. Benzyl alcohol has a retarding action towards pepsin, pancreatin, the rennet ferment, the souring of milk, and brewer's yeast.
H. W.

Temperature Sensitiveness of Saccharase (Invertase). H. VON EULER and I. LAURIN (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 24, 1—30. Compare following abstract).—The temperature-coefficient of inversion by saccharase from yeast has been determined in solution of acidity $P_H = 4.5$. The constant A of Arrhenius's temperature formula is found to be 10500 ± 500 for the range $0°$ to $20°$, and this can be taken as the inversion constant over this range. At temperatures $20°$ to $52°$, a smaller value, 8800 ± 400, is obtained. The inactivation of yeast at the optimum acidity has been determined over the range $50°$ to $65°$. Heating yeast for one hour at $59°$ reduces the activity of the saccharase by one half. The inactivation constant at this temperature is $k_c = 5 \times 10^{-3}$. For $P_H = 4.5$, the Arrhenius formula applied to the inactivation gives a constant 101000. The inactivation of saccharase has been determined for $P_H = 3$, 4, 5, and 5.7 over the range $42°$ to $55°$, and it is shown that the minimum temperature sensitiveness lies at acidities $P_H - 4—5$, that is. at the acidity of optimum enzyme activity. The Arrhenius constant is greatest in this region. The temperature sensitiveness of separated invertase is very little different from that in the yeast cells. The cell appears to exercise a slight protecting action, which allows the non-separated invertase to be heated to about $1°$ higher than the separated product. The inactivation temperature constant is a little greater for the separated invertase than for the non-separated. Invertase from bottom yeast has a smaller temperature sensitiveness than that from top yeast. The difference amounts to about $2°$, that is, the invertase from bottom yeast can be heated $2°$ higher than that from top yeast. The greater stability of bottom yeast in comparison with top yeast is not due to the presence of a protecting substance in the former, because the addition of the liquid from bottom yeast to top yeast does not increase the stability of this substance.   J. F. S.

Influence of Temperature and Acidity on the Formation of Saccharase. H. VON EULER and O. SVANBERG (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 23, 1—32).—The dependence of saccharase formation on the temperature and acidity has been investigated.

It is shown that for yeast a well-defined temperature optimum for saccharase formation lies between 26° and 30°, and that at 35° no further formation takes place. The saccharase formation is strongly dependent on the acidity of the solution. The maximum formation occurs practically at the same point as the maximum activity of the enzyme. At a greater acidity than $P_H = 2$, a disturbance of the saccharase is noticed, but even at acidity $P_H = 6$—7 a strong enzyme formation occurs, which is about 90% of that observed under the best conditions of acidity. The saccharase content of fresh living yeast is not changed by ten hours' washing with water at 10°.   J. F. S.

Diphenylarsenious Chloride and Cyanide. (Diphenylchloroarsine and Diphenylcyanoarsine.) GILBERT T. MORGAN and DUDLEY CLOETE VINING (T., 1920, 117, 777—783).

Organo-derivatives of Bismuth. III. The Preparation of Derivatives of Quinquevalent Bismuth. FREDERICK CHALLENGER and ARCHIBALD EDWIN GODDARD (T., 1920, 117, 762—773).

Physiological Chemistry.

Liquid for Determining Specific Gravity of Blood. H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, 53, lxxxiii).—Lyle's golden syrup made up with water to D 1·080 is a good substitute for the usual glycerol solution. A few c.c. of formalin solution should be added as a preservative.   J. C. D.

The Neutrality of the Blood. W. M. BAYLISS (*J. Physiol.*, 1920, 53, 162—179).—Intravenous injection of acid in sufficient quantity to neutralise half the bicarbonate in the blood does not increase the hydrogen-ion concentration of the plasma. The chief mode of compensation is by increase in pulmonary ventilation, and consequent decrease of the carbon dioxide of the blood. Renal excretion of acid, and ammonia production in the liver, do not appreciably come into play in short experiments. Injected alkali is not so readily neutralised. The chief agent in this case appears to be excretion of alkaline urine. The proteins of the plasma play no perceptible part in the maintenance of neutrality between the limits of hydrogen-ion concentration possible in the living organism, namely, below 10^{-4} or above 10^{-10} normal. No evidence was obtained that either sodium bicarbonate, serum proteins, or both together convey carbon dioxide from the tissues to the lungs. Thus the only function of the sodium bicarbonate in the blood is to regulate the hydrogen-ion concentration, whilst under normal conditions the only function of the proteins is to give a colloidal osmotic pressure and a moderate degree of viscosity

to the plasma. A simple method of determining the hydrogen-ion concentration of blood by means of indicators is described.

J. C. D.

The Reaction and Carbon Dioxide-carrying Power of Blood. I. T. R. PARSONS (*J. Physiol.*, 1919, **53**, 42—59).—By mathematical calculation, it is determined that a system composed of carbon dioxide and one other weak acid with a fixed total amount of sodium distributed between them has a carbon dioxide dissociation curve identical with that of blood. The proteins of the blood constitute the second weak acid, which shares with carbon dioxide the available sodium. The whole of the combined carbon dioxide of the blood is in the form of bicarbonate, but the proteins present in the blood confer on it a property which pure bicarbonate solution does not possess, namely, that of forming an efficient carrier for carbon dioxide.   In the blood, the "availability" of the sodium is regulated by the proteins in such a way that the carbon dioxide tends to be expelled at lower tensions, so that an efficient transport of gas is brought about.

CHEMICAL ABSTRACTS.

The Colloid-free Filtrate of Serum. A. R. CUSHNY (*J. Physiol.*, 1920, **53**, 391—398).—When serum is filtered through collodion membranes, the filtrate contains most of the crystalloid components in the same proportions as in the original serum. The only exceptions are calcium and possibly magnesium, which pass the filter in a lower concentration. Therefore the non-colloid constituents, other than these two elements, are in simple solution in serum, whilst part of the calcium and magnesium is probably in some form of combination with the proteins. J. C. D.

Metabolism of Carbohydrates. J. A. HEWITT and J. PRYDE (*Proc. Physiol. Soc.*, 1919; *J. Physiol.*, 1920, **53**, lxv; from *Physiol. Abstr.*, 1920, **5**, 79).—Experiments on the stereochemistry of certain carbohydrates in the alimentary canal indicate that the α- and β-forms of glucose are not present in a simply equilibrated aqueous solution. J. C. D.

Nitrogenous Equilibrium and Absence of Vitamines. A. DESGREZ and H. BIERRY (*Compt. rend.*, 1920, **170**, 1209—1211).—With a deficiency of vitamines, rats can be kept, for a certain time, in nitrogenous equilibrium for varying proportions of albumin. fats, and sugars, in a ration supplying sufficient energy. The minimum of albumin. fat, or sugar permissible is controlled by the chemical nature of the particular class of nutrient, and the ratio of the other two classes present. The minimum of nitrogenous nutrient necessary is reached when a sugar is present in sufficient amount in the ration. W. G.

Carrotinoids and Fat-soluble Vitamine. L. S. PALMER (*Science*, 1919, **50**, 1—2; from *Physiol. Abstr.*, 1920, **5**, 92).—The author disagrees with Steenbock's hypothesis as to the identity of carrotene and fat-soluble A. In many cases the relation breaks

down, and chickens have been raised to maturity on diets free from carotinoids. Further, certain oils (for example, cottonseed oil) are rich in carrotinoids, but are destitute of the fat-soluble vitamine. J. C. D.

The Behaviour of Basic Bismuth Nitrate towards Dilute Acids. P. W. K. BÖCKMANN (*Arch. Exp. Path. Pharm.*, 1916, **80,** 140—146).—Experiments were instituted with the object of ascertaining whether basic bismuth nitrate is capable of neutralising acids. To nitric acid of known concentration, basic bismuth nitrate was added in excess and shaken for a couple of days at 18°. The bismuth, as well as the total acid content of the filtrate, was then estimated. On the assumption that the bismuth was present in the filtrate as the normal salt, the free acid was calculated by difference. The H-ion concentration of the above filtrates was also determined colorimetrically. From the results obtained, it was concluded that at an acidity similar to that which prevails in the stomach, basic bismuth nitrate does not possess any neutralising capacity. S. S. Z.

The Effect of Injection of Guanidine on the Creatine-content of Muscle. G. M. WISHART (*J. Physiol.*, 1920, **53,** 440—445).—Intravenous or subcutaneous injections of inorganic salts of guanidine cause an increase in the creatine content of muscles. The bearing of this observation on the theories of creatine formation is discussed. J. C. D.

The Formation of Adrenaline. F. KNOOP (*Ber.*, 1920, **53,** [B], 716—718).—A further contribution to the controversy with regard to the mode of formation of adrenaline in the organism (compare Rosenmund and Dornsaft, this vol., i, 56, 327; Knoop, this vol., i, 161). H. W.

The Chemical Nature of the Bee's Poison. FERDINAND FLURY (*Arch. Expt. Path. Pharm.*, 1920, **85,** 319—339).—The author carried out some investigations on the protein-free poison isolated by Langer from the poison sac of the bee. It was found that the principle was a base of complicated constitution. By means of digestive processes, a considerable fraction of a lipoid ature was obtained from it. The following were the products of hydrolysis with hydrochloric acid: (1) a ring compound of the indole series; (2) choline; (3) glycerol; (4) phosphoric acid; (5) palmitic acid; (6) a high molecular, non-crystallisable, unsaturated fatty acid; (7) a volatile fatty acid, presumably butyric acid; (8) and a nitrogen-free fraction. The latter fraction was found to be the pharmacologically active principle of the bee's poison. According to the method of isolation, it can be obtained either as a neutral compound sparingly soluble in water or as an acid soluble in water. The author expresses the opinion that the bee's poison in the natural secretion is present as a complex compound in combination with lecithin and a basic fraction. S. S. Z.

The Nature of Excreted Arsenious and Arsenic Acids.
GEORG JOACHIMOGLU (*Arch. Exp. Path. Pharm.*, 1916, **80**, 8—24).
—The author shows that, on adding sodium arsenite to weakly
alkaline urine and extracting it with alcohol, arsenic can be estab-
lished both in the alcohol and in the residue. He therefore main-
tains that Salkowski is not justified in concluding that the arsenic
found in an alcoholic extract of urine is of an organic nature. The
author further criticises the various methods employed for the
estimation of arsenic acid in the presence of arsenious acid, and
considers that results obtained by such methods are not valid.
He shows, on the other hand, that by means of electrolysis in
alkaline solution, arsenious acid can be established with certainty
in the presence of arsenic acid. Employing this method, he
demonstrates that by injecting subcutaneously arsenic acid in dogs,
at least 16% of the arsenic is excreted in the urine as arsenious
acid.   S. S. Z.

The Nature of Excreted Arsenious and Arsenic Acids.
E. SALKOWSKI (*Arch. Exp. Path. Pharm.*, 1916, **80**, 231—235,
319—320); G. JOACHIMOGLU (*ibid.*, 317—318).—Polemical in refer-
ence to Joachimoglu's criticisms (see preceding abstract) on
Salkowski's earlier work.   S. S. Z.

**Influence of Adsorbent (especially Colloidal) Substances
on the Separation of Uric Acid and its Salts from Super-
saturated Solution.** RUDOLF KOHLER (*Z. klin. Med.*, 1919, **88**,
14; *Zentr. Biochem. Biophys.*, **21**, 354—355).—In connexion with
the work of Marc and with reference to the observations of Licht-
witz, the author has studied the influence of colloidal and other
adsorbent substances on the separation of urates from super-
saturated solutions. The conclusions deduced by Marc are essenti-
ally applicable to uric acid, but the retarding action is relatively
small. This action applies only to the beginning of the separation
and varies in a parallel manner with the adsorbability; its magni-
tude depends on the amount of substance which is added and the
reciprocal value of the degree of supersaturation. The insignifi-
cance of this effect is explained by the fact that uric acid in solu-
tion (also its salts) has such a pronounced tendency towards super-
saturation that the influence of the colloid has little relative value.
Contrary to the view of Lichtwitz, the author does not, therefore,
attach much importance to the action of colloids in holding crystal-
loids in solution in the urine and other fluids of animal origin.
Colloids are superfluous, or at least of secondary importance, in so
far as an explanation of the great solubility of uric acid in fluids
of animal origin is concerned.   CHEMICAL ABSTRACTS.

The Elimination of Taurine Administered to Man.
CARL L. A. SCHMIDT and E. G. ALLEN (*J. Biol. Chem.*, 1920,
42, 55—58).—Estimations of neutral sulphur and amino-acid
nitrogen in the urine of an individual to whom had been given
10 grams of taurine per os show a close agreement, which indicates

that taurine is not eliminated as taurocarbamic acid (Salkowski, this Journ., 1872, 1033; 1874, 1129). Administration of taurine in large doses does not result in any marked changes in the excretion of urea and ammonia.   J. C. D.

Excretion of Quinine in the Urine. M. NIERENSTEIN (Extract from Observations on Malaria, War Office, 1919, pp. 1—79).—See this vol., ii, 456.

Presence of True Mucin in Certain Urines. CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1920, [vii], **21**, 337—342).—The author has detected the presence of mucin in two samples of urine, both of which were distinctly acid in reaction.   W. P. S.

Urochrome. J. MELLANBY and C. J. THOMAS (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, xcvii).—The pigment of urine is readily absorbed by animal charcoal of good quality. After washing the charcoal with warm water to remove traces of other urinary constituents, the pigment is removed with 50% alcohol containing 0·5% sodium hydroxide. After neutralisation with sulphuric acid, the fluid is concentrated, and the greater part of the sodium sulphate removed by crystallisation. From the aqueous solution, the pigment is precipitated by alcohol, washed with ether, and dried in a vacuum. The pigment may be purified further by repeated reprecipitation. It is a brown, amorphous powder, very soluble in water, but insoluble in the usual organic solvents. It shows no characteristic absorption bands. The aqueous solution slowly dialyses through parchment. No definite evidence of its metabolic significance has yet been obtained, but its excretion is roughly parallel with that of creatinine.   J. C. D.

Physiological Radioactivity. H. ZWAARDEMAKER (*J. Physiol.*, 1920, **53**, 273—289. Compare A., 1917, i, 241).—In a large number of systems, the potassium ion may, as regards function, be replaced by all the other radioactive elements, the heavy ones as well as the light ones, provided the doses are equiradioactive. When applied simultaneously, the substances emitting α-rays and those emitting β-rays are reciprocally antagonistic. Potassium is (as a bearer of physiological radioactivity) for many cells a stimulus, which can restore and sustain function when it is brought in contact with the surface of the cells as a free, diffusible ion in the circulating fluid. A free radioactive radiation can take the place of potassium when previously the potassium is omitted from the circulation.   J. C. D.

The Theory of Narcosis. E. VON KNAFFL-LENZ (*Arch. Exp. Path. Pharm.*, 1919, **84**, 66—88).—The surface tension against air and paraffin, and the partition coefficient in oil and water of the aqueous solution of various narcotics were determined at 10°, 20°, and 30°. The alterations in the surface tension, both against air and paraffin, at the different temperatures were not proportional

to the narcotic potency. A better agreement could be established between the partition coefficient and the narcotic potency, and the author therefore maintains that Traube's objections to the lipoid theory of narcosis are not justified. The influence of the vapour of volatile narcotics on jellies was also studied, and it was found, in contradistinction to Traube's results, that not only do the vapours not promote imbibition, but they produce the opposite effect.   S. S. Z.

Relation between Chemical Constitution and Physiological Action in Local Anæsthetics. I. Homologues of Procaine.   OLIVER KAMM (*J. Amer. Chem. Soc.*, 1920, **42**, 1030—1033).—See this vol., i, 482.

Carbon Monoxide in Tobacco Smoke. H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxxii).—The positive results indicate the possibility of there being in a heavy smoker a condition of chronic carbon monoxide poisoning.
                                                                         J. C. D.

Toxicity of Some Inorganic Substances to Paramœcium. N. McCLELAND and R. A. PETERS (*Proc. Physiol. Soc.*, 1919; *J. Physiol.*, 1919, **53**, xii).—There is a slight suggestion of a periodic rise and fall in toxicity with increase in molecular weight; thus vanadium–manganese–iron–nickel–cobalt–calcium, also silver–cadmium–tin–mercury–thallium(ic)–lead, seem to form such a series. The most toxic metals are bivalent.   J. C. D.

Chemical Constitution and Physiological Action. The Toxicity of some Organic Metal Derivatives and some other Organic Substances. N. McCLELAND and R. A. PETERS (*J. Physiol.*, 1919, **53**, xv). The relation of chemical constitution to physiological action was tested by toxicity tests on *Paramoecia*. These preliminary experiments indicate that primary compounds are less toxic than secondary, that aliphatic compounds are less toxic than aromatic, and that arsenic compounds are less toxic than those of antimony.   J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation Characteristics of certain Pentose-destroying Bacteria. E. B. FRED, W. H. PETERSON, and AUDREY DAVENPORT (*J. Biol. Chem.*, 1920, **42**, 175—189).—The average limit of growth in the yeast–water medium was approximately p_H 3·6 to 4·0 in the case of xylose, dextrose, galactose, sucrose, lævulose, and lactose. Mannitol was decomposed more slowly, and

gave a limit of about p_H 4·3. Acidity measurements and observation of the volume of gas liberated give no idea of the amount of carbohydrate fermented. The pentose sugars, arabinose and xylose, form on fermentation more than 20% of normal acid, divided into almost equal amounts of lactic acid and acetic acid. Rhamnose is not attacked by these organisms. The aldo-hexoses, dextrose and galactose, yield acetic acid, lactic acid, and ethyl alcohol, but the acid formation is small as compared with that observed in the fermentation of the pentose sugars. Mannose ferments more slowly than either dextrose or galactose, and yields nearly equal quantities of volatile and non-volatile acids. The ketone sugar, lævulose, is rapidly reduced by the pentose-fermenting organisms to form mannitol, volatile and non-volatile acids and carbon dioxide being formed at the same time. The chief disaccharides are all fermented, but never completely. Raffinose and melizitose are not attacked. A number of other substances were examined. Mannitol, glycerol, salicin, and xylan are slowly decomposed; æsculin, starch, inulin, cellulose, succinic, tartaric, and citric acids are not attacked, whilst pyruvic, lactic, and malic acids ferment, giving rise to closely related acids. J. C. D.

Sensitiveness of Yeast Fermentation to the P_H Value.

H. von EULER and S. HEINTZE (Arkiv. Kem. Min. Geol., 1917, 7, No. 21, 1—21).—The fermentation of sucrose and dextrose by yeast has been investigated at 28° in the presence of hydrochloric acid of varying concentrations with the object of ascertaining the dependence of the rate of fermentation on the P_H value of the solution. The P_H value was determined by Sörensen's indicator method, and the velocity of fermentation by direct measurement of the volume of carbon dioxide evolved in a given time by 200 yeast cells. All experiments were carried out at 28°. The maximum velocity of fermentation lies at P_H 5, and this is also found when yeast-water or asparagine is added to the fermentation mixture, although in these cases the velocity is very much greater than in solutions which contain no absorbable nitrogen compound. The relative maximum velocities, expressed in c.c. of carbon dioxide evolved per hour, are: solutions without added nitrogen compounds, 75 c.c.; solutions with asparagine, 134 c.c.; solutions with yeast-water, 187 c.c. Oxalic acid and chromic acid in concentrations up to 0·025N do not act as yeast poisons, as has been frequently stated. In solutions of hydrochloric acid up to 0·01N, the influence of the chlorine ions is unimportant, as also is the influence of the non-ionised molecules, but with weak organic acids the undissociated molecules play a considerable part. J. F. S.

Nitrogen of the Cyanogen Group in Fertilisation.

R. PEROTTI (Atti R. Accad. Lincei, 1920, [v]. 29. i, 206—210).—In presence of suitable nutrient substances, such as dextrose, potassium cyanide in concentrations of the order of 0·05% serves as nitrogenous nutriment for micro-organisms of various kinds.

T. H. P.

The Properties of Colloidal Systems. IV. Reversible Gelation in Living Protoplasm. W. M. BAYLISS (*Proc. Roy. Soc.*, 1920, [*B*], **91**, 196—201).—By means of suitable optical arrangements giving an intense dark-ground illumination, it is possible to see that the apparently clear pseudopodia of *Amoeba* are filled with numerous very minute particles in Brownian movement. This affords further evidence of the hydrosol nature of simple protoplasm. By suitable electrical stimulation, this sol can be reversibly changed into the gel state, the change being shown by the sudden cessation of the Brownian movement, which recommences when the stimulation is stopped.   W. G.

Formation of Starch in Green Plants. C. RAVENNA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 148—150).—Polemical.
                                                        T. H. P.

Hydration Effects of Amino-compounds. D. T. MacDOUGAL and H. A. SPOEHR (*Proc. Soc. Expt. Biol. Med.*, 1919, **17**, 33—36; from *Physiol. Abstr.*, 1920, **5**, 102).—Experiments made on the swelling of agar and plant gums in solutions of amino-acids, both in the presence and absence of proteins. show that when the amino-acid is one which dissociates strongly, the swelling is less than in water. The reverse also holds. The concentration of hydrogen ions is not the only factor.   J. C. D.

Distribution of certain Chemical Constants of Wood over its Proximate Constituents. W. H. DORE (*J. Ind. Eng. Chem.*, 1920, **12**, 472—476).—About one-half of the furfuraldehyde-yielding groups in redwood (*Sequoia sempervirens*) is associated with the cellulose, and only a small amount with the lignin. The acetic acid-yielding groups are associated with the cellulose and to a small extent with the lignin, whilst the methoxy-groups are associated entirely with the lignin.   W. P. S.

Caltha palustris. E. POULSSON (*Arch. Exp. Path. Pharm.*, 1916, **80**, 173—183).—The chemical nature of the active principle of *Caltha palustris* (marsh marigold) was investigated. On distilling the aqueous extract of the fresh plant with sodium carbonate in steam, only ammonia was obtained. The author then had recourse to the potassium bismuth iodide method of precipitation employed by Jahns. The only base obtained in this way was choline. By precipitating the extract with phosphotungstic acid and examining the various fractions again, only choline was established. The author concludes that the traces of alkaloids and alkaloidal substances previously observed in extracts of *Caltha palustris* were choline.   S. S. Z.

Fat-soluble Vitamine. VI. The Extractability of the Fat-soluble Vitamine from Carrots, Lucerne, and Yellow Corn by Fat Solvents. H. STEENBOCK and P. W. BOUTWELL [with MARIANA T. SELL and E. G. GROSS] (*J. Biol. Chem.*, 1920, **42**, 131—152).—Fat solvents, such as ether, chloroform, and

carbon disulphide, remove little or none of the fat-soluble accessory factor from carrots; alcohol and benzene, however, remove considerable amounts. Ether, benzene, and alcohol all removed a considerable proportion of the vitamine from lucerne. The superiority of alcohol as an extracting fluid is also demonstrated in the examination of yellow maize. The vitamine extracted from lucerne with alcohol resists hydrolysis with alcoholic potassium hydroxide in the cold, and can be recovered in the carrotene fraction of the unsaponifiable matter. The xanthophyll fraction is practically inactive.   J. C. D.

Occurrence and Reactions of Anthocyanin Colouring Matters of the Beet-red Group. FERDINAND KRYZ (*Oesterr. Chem. Zeit.*, 1920, **23**, 55—56).—Members of the beet-red group of anthocyanins (Weigert, A., 1896, i, 387; Hilger and Mai, *ibid.*, 496) occur in the skins of fuchsia and cacti berries, and in the petals of scarlet cactus blooms. Fuchsia anthocyanin is insoluble in ether, chloroform, carbon disulphide, and amyl alcohol, but gives a carmine solution in acidified acetone or amyl alcohol. Potassium hydroxide or ammonia produces the characteristic yellow coloration, which becomes reddish with excess; organic acids or concentrated hydrochloric or sulphuric acid, a blackberry-red coloration, not destroyed by heat; nitric acid, a red coloration, yellow on warming; sodium carbonate, a dirty reddish-yellow coloration, bright yellow on warming; sodium hydrogen carbonate, blue coloration, green on warming; mercuric chloride, sodium hydrogen sulphite, or bleaching powder, a light yellow coloration. Cactus bloom anthocyanin is soluble in water, methyl, ethyl, and acidified amyl alcohols, and in glycerol, but insoluble in ether, chloroform, and carbon disulphide. The details given in regard to the effect of reagents on it are very similar, except that the last-mentioned reagents cause decolorisation, slowly at the ordinary temperature, immediately on warming. The colouring matter from red beet also gives these reactions, and is soluble in cold acetone. Wing cactus blooms apparently contain two anthocyanins, because the reddish-yellow extract obtained with hot acetone exhibits slight differences from the above products, whilst the red aqueous solution of the residue gives all the above reactions.   J. K.

Proteins from the Georgia Velvet Bean, Stizolobium Deeringianum. CARL O. JOHNS and HENRY C. WATERMAN (*J. Biol. Chem.*, 1920, **42**, 59—69). The Georgia velvet bean contains 26% of protein (N × 6·25). About 15% of protein is extracted by 2% aqueous sodium chloride. By fractional precipitation with ammonium sulphate, and by subsequent purification of the fractions, two globulins, designated α and β, may be separated, in yields of about 3 and 1·25% respectively. An albumin may also be isolated in yields of about 0·75%. When analysed by Van Slyke's method, the three proteins show marked differences. There is apparently no tryptophan in the β-globulin.   J. C. D.

Exosmosis of Acid Principles and Sugars from the Orange. G. ANDRÉ (*Compt. rend.*, 1920, **170**, 1199—1201).— During exosmosis, the ratio of the citric acid to the total sugars, reducing and non-reducing, which have diffused out remains constant. Similarly, the ratio of sucrose to reducing sugars is fairly constant, but in considering this ratio it must be remembered that inversion of a portion of the sucrose occurs during exosmosis.

W. G.

The Proteins of Green Leaves. I. Spinach Leaves. THOMAS B. OSBORNE and ALFRED J. WAKEMAN [with CHARLES S. LEAVENWORTH and OWEN L. NOLAN] (*J. Biol. Chem.*, 1920, **42**, 1—26).—By diluting the thoroughly ground leaves with one or two volumes of water and centrifugalising the extract at high speed, a solution of leaf proteins may be obtained. From this, impure protein substances may be precipitated by the addition of alcohol. This fraction is considerably purified from pigments and other substances by extraction with alcohol and ester, yielding a nearly colourless product containing about 14% of nitrogen, calculated on the ash free substance. At least 40% of the total nitrogen of spinach leaves is contained in colloidal protein; about one-third in substances which are soluble in water; and a comparatively small part in chlorophyll, phosphatides, and, presumably, nucleic acid. There are reasons for believing that certain of the constituents of the cell exist normally in the form of complexes. Examination of spinach leaves dried by warm air below 60° showed that their composition closely resembles that of the fresh leaves.

It is possible that the protein of the spinach leaves is in some form of combination with a substance of a pentosan nature, but confirmation of this has not yet been obtained.   J. C. D.

Action of Hydrogen Cyanide on the Organism of Plants. JULES STOKLASA (*Compt. rend.*, 1920, **170**, 1404—1407).—Micro-organisms offer a considerable resistance to hydrogen cyanide. Exposure to an atmosphere containing 2% by volume of this gas for twenty-four hours at 13—14° only slackened the development without stopping it in the case of *B. subtilis* and *B. mesentericus vulgatus* and certain phycomycetes. *Tilletia tritici* was, however, completely destroyed by exposure to such a concentration for twenty-four hours at 16°. Such an exposure in no way injured the germination of wheat, barley, or beetroot seeds, provided the seeds were freely exposed to the air for three days and stirred frequently before germination.   W. G.

General and Physical Chemistry.

Relation between the Refractivity and Density of Carbon Dioxide. P. PHILLIPS (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 225—240). —The density and refractive index of carbon dioxide have been determined at 34°, under such conditions as allowed a gradual change in density from 0·73 gram/cm.^{3} downwards, with the object of testing the validity of the Lorenz and Lorentz formula. The experiments were made by means of a small Fabry and Perot etalon, and the density values were deduced from the total amount of gas used and the volume of the containing vessel. From measurements with the mercury lines λλ 5790, 5461, and 4358 × 10^{-8}, it is shown that the reciprocal of the Lorenz and Lorentz constant is a linear function of the square of the density. For the wave length 5461 × 10^{-8}, the relation between the refractive index and the density is $(\mu^2+2)\rho(\mu^2-1)=6·581+0·1130\rho^2$.

J. F. S.

Maxwell's Relation between the Refractive Index and Dielectric Constant and a Method of Determining Ionic Charges in Crystals. M. BORN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 604—613).—On the space-lattice theory of the author, it is shown that the product of the ionic charge and the wavelength of the lattice-vibration in diatomic crystals may be expressed by the difference $D - n_r^2$, where D is the dielectric constant and n_r the nearly constant value of the refractive index between the short- and long-wave infra-red specific frequencies ("Eigenschwingungen"). By comparison with the wave-lengths of the residualrays ("Reststrahlen"), an approximation to the ionic charge is obtained which is in moderate agreement with that of the electrolytic ions.

J. R. P.

Reflection Capacities and Dielectric Constants of Insulating Solids and Liquids. H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 4—20).—The simple relation between reflecting capacity in the infra-red and the electric conductivity of metals deduced by Maxwell had been confirmed in previous experiments. The analogous relation between reflecting capacity and dielectric constant was confirmed in the case of twenty-five solid insulators with eight different wave-lengths in the infra-red. The insulating liquids examined exhibited an entirely different relation, which is explained by a theory due to Debye, that part of the abnormally high dielectric constant arises from the orientation of the electric dipoles assumed to exist in the molecules.

J. R. P.

Reflection Capacity and Dielectric Constants of some Amorphous Substances. H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 1280—1293).—Measurements made on fifteen amorphous substances, mainly glasses, led to the result that, for infra-red radiation of long wave-length, the reflection capacities are in close agreement with those calculated from Fresnel's theory from the dielectric constants for slowly varying fields. Anomalous dispersion in the region of Hertzian waves could not in any case be detected.   J. R. P.

Optical Properties of some Crystals in the Long-wave Infra-red Spectrum. I. and II. TH. LIEBISCH and H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 198—219, 876—900).—I. The reflection capacity of doubly-refracting crystals between the wave-lengths 22μ and 300μ, and the connexion between the electric and optical properties were determined. The results enable the frequency and strength of the corresponding vibrations in the space-lattice to be calculated.

II. Forty-eight crystals of different systems, excluding triclinic, were examined in the manner described in the previous abstract. The positions of the optic axes in adularia and gypsum were determined for ten different wave-lengths, and the gradual change of these axes in the direction of the axes of greatest and least dielectricity was found to be in agreement with the electromagnetic theory.   J. R. P.

Critical Study of Spectral Series. V. Spectra of the Monatomic Gases. W. M. HICKS (*Phil. Trans.*, 1920, [*A*], 220, 335—468. Compare A., 1910, ii, 86; 1912, ii, 512; 1913, ii, 810; 1915, ii, 499).—A theoretical paper in which the series relationships in the spectra of neon, argon, krypton, xenon, and radium emanation are examined mathematically. A table of spectrum constants, in which the most important numerical factors are contained, is given in the paper. The value of the oun in the various cases is neon, 14·47013; argon, 57·9209; krypton, 249·536; xenon, 611·0100; and radium emanation, 1787·024.   J. F. S.

Excitation of the Band Spectrum of Nitrogen by Electrons of Feeble Velocity. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, 170, 1380—1382).—From a spectrographic study under special conditions, it is shown that it is possible to excite the radiation of nitrogen with a critical potential of about 10 volts, the band spectrum thus being excited by electronic shock under a voltage decidedly lower than the potential of ionisation (18 volts).   W. G.

Measurements of Wave-lengths in the Spectra of Krypton and Xenon. PAUL W. MERRILL (*Bur. Standards, Bull.*, 1919, 15, 251—257; *Sci. Paper* No. 345).—This paper records photographic measurements of wave-lengths in the spectra of krypton and xenon,

principally in the red and infra-red. In krypton thirty-seven new lines were measured between 6576 Å and 8928 Å; in xenon fifty-two new lines between 6318 Å and 9162 Å. In this region there are numerous strong lines which are probably among the most important in the spectra of these elements. The xenon lines at 8231 Å and 8280 Å are especially notable. These and other lines may be of value as wave-length standards in the infra-red. Attention is called to a probable analogy between the spectra of the rare gases neon, argon, krypton, and xenon that this investigation has brought to light, which is shown in the tendency of the lines to form groups the position of which apparently has some relation to the atomic weight.   CHEMICAL ABSTRACTS.

Absorption Spectra of Metal Ammine Complexes. III. Absorption Spectra of Complex Salts of Nickel, Chromium, and Copper. YUJI SHIBATA and K. MATSUNO (*J. Coll. Sci. Tokyo*, 1920, **41**, 6, 1—37. Compare A., 1919, ii, 381; this vol., ii, 141). —The absorption spectra of a large number of chromium complex ammines, complex sulphates and oxalates, simple chromic salts and complex perchromic derivatives have been measured. Similar measurements have been made for nickel ammines, simple nickel salts, complex pyridine copper derivatives, copper ammines, and simple copper salts. The complex chromic compounds are shown to be stable in aqueous solutions and to give generally two or three sharp absorption bands. They are in every way comparable with the complex cobalt derivative as regards the absorption spectrum. The complex nickel compounds are generally unstable in aqueous solutions; the absorption spectra were, therefore, determined in ammoniacal solution. They exhibit, in every case, two absorption bands, but the absorption is much less strong than in the case of the metals previously examined. The absorption of the complex nickel compounds follows the same laws as that of the complexes of chromium and cobalt. The complexes of copper are the most labile in aqueous solution, and the anion exerts some influence on the absorption in this case. They give no bands, but there is general absorption in both the red and violet ends of the spectrum.
                                                                 J. F. S.

Ultra-violet Spectrophotometry of the Nitrophenols. FRED VLÈS (*Compt. rend*, 1920, **170**, 1242—1245). The spectrum of the nitrophenols in the region studied, λ 250 mμ to the visible spectrum, is constituted in general by three elements, namely, (1) an absolutely constant X band due to the absorption of the nitro-groups; this band appears to be formed by two components; (2) a band ϕ, sometimes uncertain, due to the phenolic radicle; (3) a band ψ, inferior to the region studied, and the origin of which is problematical. The constitution in wave-lengths of the spectrum of a compound will be given by the characteristics of the isolated components, slightly modified by coefficients which will depend on the stereochemical properties of the compound. W. G.

Absorption in Respect to the Properties of the Nitro-phenols. FRED VLÈS (*Compt. rend.*, 1920, **170**, 1316—1318).— A continuation of previous work (preceding abstract) in which it is shown that it is possible to calculate the absorption spectrum curves of the nitrophenols simply from their constitution and the properties of their constituent groups.   W. G.

Abnormal Rotatory Dispersion. G. BRUHAT (*Ann. Physique,* 1920, [ix], **13**, 25—48).—The first part of the paper is a mathematical discussion of the general conditions which a spectropolarimeter should satisfy. The second part is a study of certain coloured tartrates, uranyl tartrate, didymium tartrate in ammoniacal solution, and the cobalt tartrates. The results obtained confirm Natanson's law and the law previously enunciated by the author (compare A., 1915, ii, 302, 503).   W. G.

Photochemical Activity of Absorbed Radiations. CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 3, 1—35; from *Chem. Zentr.*, 1920, i, 722).—The law of critical activity explains the peculiar fact observed by Warburg (this vol., ii, 210) that the "specific photochemical effect" is of the same order of magnitude for a series of very dissimilar processes. By its aid, the sensitiveness towards light of a particular reaction can frequently be approximately estimated when only its temperature-coefficient in darkness is known. It also affords a ready explanation of the generally observed small temperature-coefficients of photochemical processes and of their increase with increasing wave-length, and also indicates the possibility of chemi-luminescence. It possibly also explains the empirical observation that a process is more susceptible to optical sensitivation for a given wave-length when it is least sensitive to this wave-length.   H. W.

Energy-changes during Photochemical Reactions in Gases. IV. Influence of the Wave-length and Pressure on Photochemical Ozonisation. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 872—885. Compare A., 1911, ii, 834; 1912, ii, 315; 1913, ii, 652).—The amount of ozone produced in oxygen by ultraviolet light of wave-length $0.253\,\mu$ is smaller, per calorie absorbed, than with light of wave-length $0.209\,\mu$. It is smaller under a pressure of 300 kg. per sq. cm. than under a pressure of 125 kg. per sq. cm. Both results are in contradiction to Einstein's law of photochemical equivalence, which requires considerable modification to accord with experiment. Of the original assumptions of Einstein, (1) that only one quantum is absorbed, (2) that all absorbing molecules are decomposed, the first may for the present be retained, but the second may be modified by assuming that only a portion of the absorbing molecules are decomposed.   J. R. P.

Energy-changes during Photochemical Reactions in Gases. V. Absorption of Ultra-violet Radiation by Oxygen. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 230—242).—Between pressures of 30 to 400 atm., large deviations

from Beer's law were found. The molecular absorption of oxygen increases appreciably with the pressure. The increase is greater for the shorter ($0\cdot209\,\mu$) than for the longer ($0\cdot253\,\mu$) of the waves used, and was greater in pure oxygen than in mixtures of oxygen and nitrogen. The deviations are explained by a theory of K. Ångström (*Arkiv. Math. Astron. Fysik*, 1908), according to which they are due to molecular collisions, and are represented by formulæ.   J. R. P.

Energy-changes during Photochemical Reactions in Gases. VI. Photolysis of Hydrogen Bromide. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 314—329).—The photolysis of hydrogen bromide by the wave-lengths $0\cdot209\,\mu$ and $0\cdot253\,\mu$ follows Einstein's law of photochemical equivalence; the photochemical action per unit of energy absorbed increases with the wave-length, and nearly in the ratio required by the theory. The law can hold only when the work required in the decomposition of the molecule is smaller than the quantum of the decomposing radiation. This relation is fulfilled with hydrogen bromide with the two wave-lengths used, but is not fulfilled in the photolysis of ammonia by the wave-length $0\cdot209\,\mu$ and of oxygen by the wave-length $0\cdot253\,\mu$. The deviations found in the last two cases are therefore explained.   J. R. P.

Energy-changes during Photochemical Reactions in Gases. VII. Photolysis of Hydrogen Iodide. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 300—317).—The fulfilment of Einstein's law of photochemical equivalence was demonstrated with hydrogen iodide with the wave-lengths $0\cdot207\,\mu$, $0\cdot253\,\mu$, and $0\cdot282\,\mu$.   J. R. P.

Energy-changes during Photochemical Reactions. VIII. Photolysis of Aqueous Solutions and the Law of Photochemical Equivalence. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 1228—1246).—Aqueous solutions of nitrates of alkalis and alkaline earths are converted by photolysis into nitrites. The specific photochemical action is considerably greater in weakly alkaline than in weakly acid solutions, increases with the concentration of nitrate, and is greater for shorter than for longer waves, in contradiction to Einstein's law of photochemical equivalence.   J. R. P.

Energy-changes during Photochemical Reactions. IX. Photochemical Transition of Isomerides. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 960—974).—The conversion of maleic into fumaric acid under the influence of wave-lengths $0\cdot207\,\mu$, $0\cdot253\,\mu$, and $0\cdot282\,\mu$ in aqueous solutions was studied. The results indicated that the extension of the law of photochemical equivalence (see IV, this vol., ii, 404) does not lead to quantitative results, but serves as a guide to the theoretical interpretation of the experiments.   J. R. P.

Photochemical Dissociation of Ferric Chloride. ERNESTO
PUXEDDU (*Gazzetta*, 1920, **50**, i, 154—161).—Exposure to direct
sunlight of a dilute solution of ferric chloride in pure anhydrous
ether results in almost instantaneous reduction of the salt to
ferrous chloride. No reversion of this reaction occurs in the dark,
the chlorine liberated during the reduction being completely used
up, partly in chlorinating the ether, apparently to a mixture of the
dichloro- and trichloro-derivatives, and partly in oxidation processes,
with formation of aldehydes; the latter undergo polymerisation to
some extent.

In moderately concentrated ethereal solution, ferric chloride is
slowly reduced to a mixture of ferrous chloride and a brownish-
black organic iron compound containing 2·8% of the metal, and
only if this compound is gradually removed is complete reduction
possible.   T. H. P.

The Disruption of Atoms by α-Rays. G. S. FULCHER
(*Science*, 1919, **50**, 582—584).—In Rutherford's recent papers on
the nuclear bombardment of light atoms by α-particles, he finds
that the ranges of the swiftly accelerated nitrogen and oxygen
atoms correspond fairly closely with those to be expected if the
swift particles consisted of the singly charged nitrogen and oxygen
atoms. The author points out that this requires that the other
outriding electrons should accompany the parent atom in its swift
motion, which is open to twofold objection. First, a velocity
approaching 10^9 cm. sec.$^{-1}$ could not be imparted to the electrons
in less than 10^{-18} sec. The strength of the field not being great
enough to overcome the inertia of the electrons, they would be left
behind initially. Secondly, admitting that the first contention is
wrong, the author believes that the outriding electrons would soon
be brushed off by the large number of atoms encountered in the
long range of flight. As an alternative, the possibility is suggested
that the nitrogen atom, presumably composed of hydrogen and
helium atoms, is entirely disrupted, and that the particles observed
by Rutherford are really doubly charged helium atoms or
α-particles. The additional energy necessary to give them a range
greater than that of the initial bombarding α-particles would come
from the internal energy of the atom in the moment of its disrup-
tion, and the phenomenon would constitute a type of artificially
produced radioactivity. One difficulty of the author's assumption
is to account for the large number of particles which take the same
direction as the initial α-particles. He believes this difficulty will
not prove insurmountable. Examination of the e/m value of the
particles will determine whether Rutherford is correct.
                                                    CHEMICAL ABSTRACTS.

X-Ray Spectra of the Elements. R. WHIDDINGTON (*Phil.
Mag.*, 1920. [vi], **39**, 694—696).—A theoretical paper in which the
speed of the electron (v) carrying the same energy as the α-lines in
the K and L spectra of the elements is shown to be fairly well
represented by the formula $v = C . N + D$, where N is the atomic

number of the element and C and D are constants determined by the series. For the K series $v = 2(N-2)10^8$ cm./sec., and for the L series $v = (N-15)10^8$ cm./sec. The values of $v \times 10^{-8}$ and $2(N-2)$ and $v \times 10^{-8}$ and $(N-15)$ are compared, respectively, in the K series (nine elements) and in the L series (seven elements), when a very fair agreement is obtained.

J. F. S.

The Fine Structure of X-Ray Spectra. M. DE BROGLIE (*Compt. rend.*, 1920, **170**, 1245—1246).—As in the case of the X-ray spectrum of tungsten (compare this vol., ii, 344), it is found that the rhodium spectrum contains a ray which really consists of two components, for which $d\lambda = 0.0006$ Ångström.

W. G.

Spectrum of X-Rays from an Aluminium Target. W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 389—393).—The general radiation spectrum of aluminium for wave-lengths from 0.1820×10^{-8} to 1.259×10^{-8} cm. has been carefully examined for characteristic radiation which might belong to the J-series of short wave-lengths found by Barkla. No characteristic radiation was found that could not be attributed to molybdenum from the tube or lead from the jaws of the slit. CHEMICAL ABSTRACTS.

X-Ray Absorption Frequencies Characteristic of the Chemical Elements. WILLIAM DUANE and KANG-FUH-HU (*Physical Rev.*, 1919, **14**, 516—521).—The critical absorption frequencies in the K-series for the elements from bromine ($N=35$) down to manganese ($N=25$) were measured. Using these and other data, it is shown that for the elements from cerium to magnesium the square root of the critical frequency is not quite a linear function of the atomic number, N. The deviations amount to several units %. However, the critical velocities, calculated from the quantum relation $\frac{1}{2}mv^2 = hv$, using the transverse relativity mass $m = m_0[1 / \sqrt{1 - (v/c)}]$, are found to be linear with N to within about one-fifth %.

CHEMICAL ABSTRACTS.

X-Ray Absorption Frequencies Characteristic of the Chemical Elements. W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 522—524).—The measurements of critical K absorption frequencies for the elements from lead ($N=82$) to neon ($N=60$) were made. The deviation from linearity of the sq. root of the frequency with N is much greater than for the lighter elements. This is also true of the deviations of the critical velocity as measured by Duane and Kang-Fuh-Hu (preceding abstract).

CHEMICAL ABSTRACTS.

Relation between the Intensity of General X-Radiation and the Atomic Number of the Anticathode. W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 525—529).—The intensity of the general X-radiation from the four elements iron, cobalt, nickel, and copper was measured and found to be proportional to the atomic number rather than to the atomic weight.

These four elements were chosen because, in the case of nickel and cobalt, the atomic weight and atomic number are in reverse order.
CHEMICAL ABSTRACTS.

Crystallisation of a Radium Barium Solution. CLARENCE E. SCHOLL (*J. Amer. Chem. Soc.*, 1920, **42**, 889—896).—Crystallisation of the systems radium chloride–barium chloride and radium bromide–barium bromide are considered theoretically, and a number of experiments based on the theoretical results described. On cooling a saturated solution of the chloride from 100° to 0°, one-half of the total chlorides separates, whilst one-third of the bromides separate under similar conditions. The concentration of radium in any dish in the positive direction is given by $C = A K^n$, where C is the concentration, A the known concentration of the dish at the start, K the factor of enrichment, and n the number of recrystallisations. The concentration of any dish in the negative direction is $C' = A'(X - K)^m/(X - 1)^m$, where X is the inverse fractional proportion of the total weight of material occurring as crystals, and m the number of crystallisations in the negative direction. In the case of the chlorides, 50% of the material separates from 0·5N-hydrochloric acid solution, which gives a factor of enrichment of 1·62. Hence $C = A \times 1·6^n$ and $C' = A \times 0·4^m$. Crystallising so that the crystals move one dish forward and the liquors two dishes backward, a concentration is effected as follows: if 1·0 be the radium concentration of the starting dish, that of the fifth dish to the right has a concentration of 10·6, whilst the eighth dish to the left has a concentration of 0·026. In the bromide system, one-third the material separates from saturated solutions of 0·33N-hydrobromic acid, and the enrichment factor is 2·49. Hence $C = A \times 2·49^n$ and $C' = A \times 0·25^m$. Crystallising so that the crystals go two dishes to the right and the liquors three dishes to the left, the following concentration is obtained. If the radium concentration in the starting dish be 1·0, then the ninth dish to the right has a concentration of 62, and the ninth dish to the left has a concentration of 0·016. Hence the bromide system is more efficient than the chloride system. Several other systems are described.   J. F. S.

Concentration of Radium and Mesothorium by Fractional Crystallisation. JOHN L. NIERMAN (*J. Physical Chem.*, 1920, 24, 192—200).—A number of crystallisations of barium bromide containing radium bromide and mesothorium bromide have been carried out in neutral solutions and in solutions in hydrobromic acid of various concentrations with the object of ascertaining the conditions under which the optimum crystallisation factor is obtained. By crystallisation factor, the author understands the ratio of radioactive bromide in the crystals to that in the substance before crystallisation. The results show that this factor is independent of the concentration of the hydrobromic acid. The crystallisation factor is given for various percentages of salt separating; thus, when 24·3% of the salt separates, the factor is

2·43, and this decreases with increasing separation to 1·44, when 69·0% separates. For concentrations of mesothorium up to 2 mg. per gram of salt, the crystallisation factor remains constant. The separation of mesothorium and radium from barium can be carried out advantageously in either neutral or dilute acid solutions of the bromides. All measurements of activity were made by means of the γ-ray. J. F. S.

The **Conductivity of Permutite Mixtures.** V. ROTHMUND and G. KORNFELD (*Zeitsch. anorg. Chem.*, 1920, **111**, 76—77).— Polemical. A reply to A. Günther-Schulze (A., 1919, ii, 490). E. H. R.

Form of the Conductivity Function in Dilute Solutions. Correction. C. A. KRAUS (*J. Amer. Chem. Soc.*, 1920, **42**, 990 –991. Compare this vol., ii, 217).—Several of the equations previously published have been corrected. J. F. S.

Electrolytic Potential of the Change Nitrite → Nitrate + Nitric Oxide. The Energetic Relationships of the Most Important Compounds of Nitrogen with Oxygen and Hydrogen. HANS PICK (*Zeitsch. Elektrochem.*, 1920, **26**, 182—196).--A theoretical paper in which it is shown that the normal potential of the change $2NO_2' \rightarrow NO + NO_3'$ at 25° may be calculated from the electrometric measurements of Moore (A., 1913, ii, 467), and the value + 0·49 volt obtained. This value is also obtained from the chemical measurements of the equilibrium of the decomposition of silver nitrite (Abegg and Pick, A., 1906, ii. 833). Using this normal potential, the equilibrium measurements of Lewis and Edgar (A., 1911, ii, 264) for the chemical decomposition of nitrous acid into nitric oxide and nitric acid, the energetic relationships between the substances NO_3'. NO_2', NO, and HNO_2 are calculated for 25°, and the results expressed as normal potentials. From thermodynamic relationships and from equilibrium data previously published, the energetic relationships are deduced and expressed as normal potentials for the substances N_2, N_2O, NH_3, NH_4'. NO_3, N_2O_4. The normal potentials thus calculated are compared with known chemical and electrochemical data and found to be in good agreement. J. F. S.

Photoelectric Investigations with Salt Solutions. TORSTEN SVENSSON (*Arkiv. Kem. Min. Geol.*, 1917, **7**. No. 19, 1—142).— The change of *E.M.F.* occasioned by illuminating one side of a cell, of the type Pt [soln.''soln.|Pt. by ultra-violet light whilst the other half is dark, has been measured for solutions of potassium and cobalt chlorides, cobalt ammonium sulphate, nickel, cobalt, manganese, chromium, zinc, magnesium, copper, and potassium sulphates, sulphuric acid, hydrochloric acid, mixtures of potassium chromate and sulphuric acid, potassium ferricyanide and potassium hydroxide, and potassium ferrocyanide, potassium ferricyanide, and potassium hydroxide. All measurements were made

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over prolonged intervals, and the solutions were stirred by a fine stream of nitrogen. The measurements were made both with the electrode illuminated and unilluminated. It is shown that in most cases the $E.M.F.$ towards an indifferent electrode changes on illumination. The change depends on the nature of the salt, and after the illumination ceases, the $E.M.F.$ changes in the direction of the value which the solution previously possessed. Both positive and negative changes of $E.M.F.$ are observed, and, in consequence, maxima and minima, as well as inflexion points, are found in the potential–time curves. The theoretical formula

$$E = \rho k L B / (kL + k_1)[1 - e^{-(kL+k_1)t}] - \rho k_2 L_1 B_1 / (k_2 L_1 + k_3)[1 - e^{-(k_2L_1+k_3)t}]$$

has been tested by the results obtained with the simple salt solutions and found to be generally obeyed. The nitrogen used is shown to have no other effect than that of a stirrer, and the photo-electrical effect is shown not to be due to the formation of ozone or hydrogen peroxide. The illumination of the electrode is also unnecessary for the production of the potential change. In the case of nickel sulphate, the effect of the light intensity is shown to be in accordance with the formula

$$E = \rho k L B \,(kL + k_1)[1 - e^{-(kL+k_1)t}].$$

The effect is either proportional to the concentration or entirely independent of the concentration, depending on the relationship between the concentration and the intensity of illumination. Experiments with mixtures of potassium dichromate and sulphuric acid showed that the potential increased on illumination, whilst with the substances alone it decreased. In the mixtures, the effect was at first negative, but soon changed to a strong positive effect. Here also the illumination of the electrode is without effect, and the change of $E.M.F.$ is occasioned by the ultra-violet light waves, which are absorbed by glass. The change of $E.M.F.$ in these cases is independent of the concentration, but depends on the composition of the mixture, the maximum effect being obtained with a solution containing 75 mols. % of potassium dichromate. The $E.M.F.$ returns to the original value when the light is removed with a velocity which depends on the composition of the solution, and is greatest for pure sulphuric acid. Solutions of potassium ferrocyanide in alkaline solution, on illumination showed at first a decreased $E.M.F.$, which rapidly changed to an increased value. In mixtures of ferrocyanide and ferricyanide in alkali, the velocity of the change of potential is greater the larger the amount of ferricyanide present. Experiments with Röntgen rays gave an effect of the same nature, but much smaller than that observed with ultra-violet light. Theories are put forward to explain the effects observed. An historical summary of the work already published on this subject is included in the paper.   J. F. S.

The Theory of Electrolytic Ions. XIV. Kohlrausch's Law of Additivity. RICHARD LORENZ (*Zeitsch. anorg. Chem.,* 1920. **111**, 55 –75).—The work of Bjerrum (A., 1919, ii, 9) and

others indicates that strong electrolytes in dilute solution are completely dissociated. The molecular conductivity, μ, can be expressed by the equation $\mu = aF(U + V)$, where a is the degree of dissociation, F the constant of Faraday's law, and U and V the ion mobilities, which are supposed to be invariable. Since the conductivity, μ, with decreasing concentration approaches a limiting value, μ_0, it follows that, if dissociation is already complete, U and V must be variable, and must approach limiting values, U_0 and V_0. A new equation is obtained, $\mu = F(xU_0 + yV_0)$, where x and y are mobility coefficients. According to the old theory, the transport number, n, is given by $n = U/U + V$, and is a constant, independent of the degree of dissociation, a. In terms of the new theory, however, where, instead of variable degree of dissociation, variable ionic mobility is assumed, the transport number also becomes variable, namely, $n = xU_0/(xU_0 + yV_0)$. The transport numbers can only be equal when the mobilities of the two ions (in the case of electrolytes dissociating into two simple ions) are equal, for it is shown that the rate of change of mobility with concentration is the same for all ions. In the cases of potassium chloride, bromide, and iodide, the mobilities of all the ions are approximately equal at the same concentration, and consequently the transport numbers are practically constant for all concentrations. The mobilities and transport numbers of the ions have been recalculated for the salts potassium chloride, bromide, iodide, nitrate, nitrite, chlorate and thiocyanate, and sodium chloride, nitrate and iodate, and the values of the mobility-coefficients of the potassium, sodium, and chlorine ions at different concentrations are tabulated.

E. H. R.

Cadmium-Vapour Arc Lamp. Henry J. S. Sand (*Phil. Mag.*, 1920, [vi], **39**, 678--679).---An answer to Bates's criticism of the cadmium vapour arc lamp (this vol., ii, 221). The author points out that the difficulties experienced were due in all probability to faulty pumping and to the presence of oxide formed by traces of water vapour.
J. F. S.

Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature. Rudolf Mewes (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1920, **12**, 10--13; from *Chem. Zentr.*, 1920, i, 694--695).---In continuation of previous investigations (this vol., ii, 227), the author shows that the assumptions underlying the considerations of ideal gases are no longer tenable, and must be replaced by new hypotheses. The experiments, which improve the older ideas, confirm the equations which have been proposed by him.

Gay-Lussac's law is only valid for nitrogen at the atmospheric pressure, and does not hold for increased or decreased tensions. Conversely, the discrepancies from Mewes's summation law increase greatly with increasing initial pressure. It is found that this phenomenon can be explained by a consideration of the effects of surface condensation and the action of mass. The influence of

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surface condensation and partial liquefaction becomes less marked as the tension to which the gases are brought by cooling decreases. For this reason, the densities of gases at low temperatures can be most accurately estimated by observing the change of tension with diminishing temperature, as has been demonstrated by a series of unpublished experiments.   H. W.

Specific Heat of Saturated Vapour and the Entropy Temperature Diagrams of certain Fluids. (Sir) J. A. EWING (*Phil. Mag.*, 1920, [vi], **39**, 633--646).—A theoretical paper in which the change in the value of the specific heat of a saturated vapour, K_s, with temperature is considered. In the case of steam the value is negative, whilst with ether it is positive. It is shown that $K_s = Td\phi_s/dT$, where ϕ_s is the entropy of the saturated vapour, and consequently the value of K_s is negative under all conditions that make the entropy of the vapour increase with decreasing temperature. It is negative so long as the entropy temperature line for saturated vapour slopes down to the right; this form of curve is found for steam, carbon dioxide, and ammonia, and may be termed the normal curve. If the curve slopes in the opposite direction, the value of K_s is positive, and this type of curve is found for ether, benzene, ethyl propionate, and acetic acid. The entropy–temperature diagrams are drawn from known data for ethyl alcohol, propyl alcohol, ethyl ether, benzene, ethyl propionate, and acetic acid.   J. F. S.

Specific Heats and Heats of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes. Correction. J. NARBUTT (*Zeitsch. Elektrochem.*, 1920, **26**, 203—204).—A long list of corrections of formulæ and numerical data which occur incorrectly in the author's papers on the above-named subject (A., 1919, ii, 215. 216, 217).   J. F. S.

Vapour Pressure and Heat of Vaporisation. J. J. VAN LAAR (*Rec. trav. chim.*, 1920, **39**, 371--410. Compare this vol., ii, 287).—A theoretical, mathematical discussion of these two physical properties.   W. G.

Surface Condensation Error in certain Measurements of Vapour Pressure by the Gas Current Saturation Method. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1920, **42**, 978—985). —The condensation of water from its saturated vapour in air on a water-washed and steamed glass surface and on an acid-washed, steamed, and water-washed asbestos surface has been investigated under the conditions which generally obtain in the use of the gas-current saturation method of vapour-pressure measurement. In the case of glass wool, the condensation amounts to 0·012–0·127 mg. per sq. cm. of glass surface at 22°, whereas asbestos takes up about 28—32% of the water from the saturated air. This quantity of deposited water is sufficiently large to explain the many un-

explained irregularities recorded in the literature of measurements of vapour pressure by this method.

J. F. S.

The Manipulation of Volatile Substances. IV. ALFRED STOCK [with ERNST KUSS and KARL SOMIESKI] (*Ber.*, 1920, **53**, [*B*], 751—758. Compare A., 1914, ii, 171; 1917, ii, 442; 1918, ii, 353).—In the estimation of tension in the vacuum apparatus, it should be noted that a certain amount of fractionation occurs in the case of mixtures, whereby the vapour becomes richer than the residue in the volatile constituent. This factor is particularly important when only small quantities of material are available; undue reduction in the size of the apparatus is impracticable, and the experimental results must be interpreted with caution. In estimating the tension of solid substances, it is better to cool the regulating bath to the required temperature or to warm the substance somewhat above the experimental temperature before bringing it into the bath; with the reverse procedure, the temperature only becomes slowly uniform throughout the mass, and the tension registered is that of the coldest portion of the substance.

Fractional distillation is only advantageous in dealing with liquid substances. Solids should therefore be distilled under such pressure that they first liquefy. The receiver should be so cooled that a difference in tension of only a few millimetres exists between the substance under distillation and the distillate. Constant movement of the liquid is advisable, and for this purpose a special apparatus is described and figured; this consists essentially of a small induction coil with a simple interrupted and oscillating core. It is attached to the apparatus in the neighbourhood of the distillation vessel, and keeps the whole apparatus, and therefore the liquid, in steady vibration.

The Gaede rotary mercury–air pump previously used is now replaced by the Volmer mercury vapour pump, a Gaede rotary oil pump being used as accessory, whilst the gases are drawn off by an automatic Töpler pump. An improved automatic valve for use in connexion with the latter is described and figured.

The provision of suitable cooling baths for temperatures slightly above that of liquid air has previously been a matter of difficulty; it is now found that liquid propylene (b. p. –48°) fulfils the required conditions admirably, since it has an extraordinarily low melting point and remains highly mobile at the temperature of liquid air; a disadvantage, however, lies in its gaseous nature at the ordinary temperature. The direct introduction of liquid air into the cooling liquids is to be avoided, on account of the violence of its evaporation and also the unevenness of the induced cooling; the latter drawback is also noticed with baths in which the liquid air is allowed to evaporate in coils immersed in the cooling liquid. A special type of cooling vessel is figured which avoids these disadvantages; the liquid air is brought into a copper cylinder immersed in the cooling bath. Its effect is controlled and uniform, since cooling occurs from above downwards, whilst the metal tends

to equalise the temperature. For extremely low temperatures, the use of a heavy, cylindrical aluminium block is recommended; in this, four holes are bored. One of these serves for the introduction of liquid air, and, to avoid the spurting of the latter, is shielded from the remainder by a vulcanite partition. The remaining holes are used for the insertion of thermometers, substance under investigation, etc. The block may be insulated by being suspended in a Dewar vessel. By regulation of the pressure of the air, the temperature of the block may be kept constant to within a fraction of a degree for long periods. Equalisation of temperature between the metal and the thermometers, etc., may be hastened by filling the holes with liquid propylene, but this is only necessary in the case of extremely accurate experiments. The use of aluminium is particularly advantageous, since at low temperatures the metal has a low specific heat and an extraordinarily high conductivity for heat.   H. W.

Thermal Capacity of Water between 5° and 50°. W. JAEGER and H. VON STEINWEHR (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 424--432).—The 15° calorie is found by refined electrical heating measurements to be equivalent to 4·184 international watt-seconds. The minimum specific heat of water occurs at 33·5°.   J. R. P.

The Properties of Fluids in the Neighbourhood of the Critical Point and the Characteristic Equations. G. BRUHAT (*Compt. rend.*, 1920, **170**, 1173--1175).—A mathematical discussion of the subject, with special reference to the equations of van der Waals and Clausius.   W. G.

Absolute Entropies of Monatomic Substances. MAX PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 653—667).—From the equations of statistical mechanics, the characteristic thermodynamic functions are derived for a single atom moving freely in a hollow sphere and in a hollow, rectangular parallelopiped. The calculation is then extended to a monatomic gas, and it is shown that the degrees of freedom corresponding with the separate atoms must be incoherent. The expression of Nernst (*Verh. Deut. Physikal. Ges.*, 1916, **18**, 83) for the energy of a gas is discontinuous in respect of temperature, so that a definite value of the specific heat cannot be found. Those deduced by Stern and Tetrode are identical with that found in the present paper, with the exception of an additive constant.   J. R. P.

Relationships between Critical Data and other Properties of Organic Liquids. W. HERZ (*Zeitsch. anorg. Chem.*, 1920, **111**, 52—54. Compare A., 1920, ii. 285).—It has been shown that, for a large number of non-associated organic compounds, the quotient of the critical temperature, T_k, and the critical pressure, p_k, divided by the sum of the valencies of the constituent atoms ($C=4$, $H=1$, $O=2$, and $N=3$), is approximately a constant, 0·45.

From the known relationship between critical volume, temperature, and pressure, it follows that $v_k/z = \text{const.}$, where v_k is the critical volume and z the sum of the valencies. This is shown to be the case for a number of esters, ethers, and hydrocarbons, the value of the constant varying between 0.00038 and 0.00047. It is also deduced that the value of the heat of vaporisation, L, can be found from the expression $L = T_s/0.45d_kz$, where T_s is the boiling temperature (abs.) and d_k the critical density. The molecular refraction, $MR = 1.8T_k/p_k$, can be written $MR = 0.8z$. Since, however, the molecular refraction depends also on the constitution of the compound, the values calculated from the formula are only approximate.   E. H. R.

Comparative Method for Determining Vapour Densities. PHILIP BLACKMAN (*J. Physical Chem.*, 1920, **24**, 225—229).—Two glass bulbs made of graduated burette tubing and about 10 cm. long are joined together by capillary tubing. The free ends are narrowed and drawn out into tubes of sufficient diameter to admit small weighing tubes. The apparatus is placed upright and half filled with mercury. The substances the vapour densities of which are to be compared are weighed out in very small quantities (0.02—0.10 gram) in narrow glass tubes and placed one in each bulb. One of the bulbs is then sealed at the top, and, when cooled to a known temperature, the difference in the height of the mercury levels is noted and the positions of the mercury level also noted, so that later the volume of air (V) in the sealed bulb may be determined. The other bulb is then sealed, and the same measurements : mercury levels again taken, so that the volume of air (V_1) may e determined. The apparatus is now placed in a deep beaker, overed with a suitable liquid, and heated to a temperature afficiently high to vaporise completely both liquids. Again the mercury levels are determined, so that v_1 and v_2, the volume of ir and vapour in the two tubes, may be determined. The apparatus is now inverted, and the graduated tube cut away from the horizontal connecting tube, and the volumes, V, V_1, v_1, and v_2 determined by filling with mercury from an accurate burette to the observed levels. Four approximate formulæ for calculating the vapour density are given, which are applied to measurements with acetone, diethyl ether, chloroform, and ethyl alcohol. The results are very good.   J. F. S.

Some Consequences of the so-called Deterioration Theory l Gases. W. NERNST (*Sitzungsber. Preuss. Akad. Wiss., Berlin,* 119, 118—127). At very low temperatures, the ordinary gas law, $v = RT$, is replaced by the equation $p = (R/V) \cdot \beta v \cdot (1 - e^{-\beta v/T})$, there $\beta = 4.863 \cdot 10^{-11}$; $v = h.N^{\frac{1}{2}}.4\pi m/V^{\frac{1}{3}}$, where $N = 6.17 \cdot 10^{23}$, $= 6.55 \cdot 10^{-27}$, $m = $ mass of molecule. For $T = 0$, this leads to a pressure at the absolute zero, $p = h^2.N^{\frac{4}{3}}/4\pi m V$. This pressure is assumed to be due to directed repulsive forces analogous to valency acting between the molecules, which are inversely proportional to

the cubes of the distances. These will be appreciable only at extremely small distances, that is, at very low temperatures. The theory leads to the following equation for the viscosity at very low temperatures, $\eta = m^3 u^3 / 9h^2$, where u is the molecular velocity. The connexion between viscosity and temperature required by the theory is approximately fulfilled by the measurements on hydrogen at the lowest temperatures. The result is an indirect confirmation of the " deterioration theory " proposed by the author.   J. R. P.

Compressibility and Viscosity of Water and of its Solutions, and its Polymerisation. STEFANO PAGLIANI (*Gazzetta*, 1920, **50**, i, 186—194).—The author discusses the work of Richards and Palitzsch (A., 1919, ii, 97), Pagliani and Palazzo (*Atti R. Accad. Sci. Torino*, 1884, **19**), Pagliani and Vicentini (*Mem. Accad. Lincei*, 1884, **19**), Pagliani (*Rend. R. Accad. Lincei*, 1889, **5**), Tait (*Proc. Roy. Soc. Edin.*, 1882, **12**), Tammann (A., 1910, ii, 495), van Laar (A., 1900, ii, 189), Bousfield and Lowry (A., 1910, ii, 842), Battelli (*Atti R. Accad. Sci. Torino*, 1885, **20**), and Pagliani and Oddone (*Atti R. Accad. Sci. Torino*, 1887, **112**), and draws the conclusion that the hypothesis of the polymerisation of water serves to explain most of the observations made on water and aqueous solutions with reference to their compressibility and viscosity, and to the variations of these with change of temperature, pressure, and concentration of the solutions.   T. H. P.

The Viscosity of Colloidal Solutions. PAUL BARY (*Compt. rend.*, 1920, **170**, 1388—1390).—If a unit volume of dry colloid is swollen by a volume, a, of liquid, Einstein's formula for the viscosity may be written $a = (\eta - 1 - 2 \cdot 5 v_0) / 2 \cdot 5 v_0$, where η is the viscosity of the colloidal solution, that of the pure medium being taken as unity, and v_0 is the amount of colloid in unit volume. This gives a means of determining the coefficient of swelling by viscosity measurements. It is shown that colloids which enter into suspension in a given medium without any external agency yield liquids in which the colloid shrinks progressively with the time to a degree which depends on the concentration and the temperature. This shrinking is accentuated by dilution, and tends towards zero for zero concentration.   W. G.

Adsorption of Hydrogen by Quartz at Low Temperatures. G. R. PARANJPE (*Proc. Asiatic Soc. Bengal*, 1919, **15**, cxxxvi—cxxxvii).—An apparatus based on the principle of the differential manometer was used. Differences in pressure due to unequal adsorption in the two bulbs were measured by the volume change necessary to re-establish equilibrium. The measurements were made at $-190°$ and at pressures from 25 to 350 mm. The volumes of hydrogen adsorbed at these pressures by 100 sq. cm. of quartz surface, corrected to normal temperature and pressure, were $2 \cdot 0$ c. mm. and $10 \cdot 5$ c. mm. respectively. The results were used in calculating the correction for a hydrogen thermometer of quartz.

Even at this low temperature the correction is very small. Work with other gases and at other temperatures is in progress.

CHEMICAL ABSTRACTS.

Adsorption of Sulphur Dioxide by the Gel of Silicic Acid.
JOHN McGAVACK, jun., and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1920, **42**, 946—978).—The adsorption of sulphur dioxide by silicic acid gels has been measured at 100°, 80°, 57°, 40°, 30°, 0°, −33·4°, −54°, and −80°. The effect of the water content of the gel was determined by using gels containing 2·31, 3·51, 4·86, and 7·97% of water respectively. It is shown that the maximum adsorption is exhibited by gels containing about 7% of water. The adsorption is shown to be reversible in all cases in the absence of air. In the presence of small amounts of air, the rate of adsorption was greatly decreased, and adsorption and desorption were irreversible. The empirical equation of Freundlich was found to hold over almost the entire range studied, exceptions being at those points where the saturation pressure was approached. The equation $V/\sigma^{1, n} = K(p/p_0)^{1/n}$ is found to hold, where V is the uncorrected volume of the condensed phase, σ the surface tension, p the pressure of the gas phase, p_0 the vapour pressure of the liquid, and K and $1/n$ constants dependent on the physical properties of the adsorbent.   J. F. S.

Sorption of Vapours by Charcoal. BROR GUSTAFSON (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 22, 1—17).—The sorption of vapours of water and acetic acid by charcoal has been examined at a series of pressures (4·6—17·4 mm.) and at temperatures 16·5—20°. In the case of water vapour, it is shown that for small pressures the amount of sorption is proportional to the pressure, and the sorption in these cases must consist in the formation of a solid solution; at pressures from 6—7 mm., the strict absorption commences. On producing the solution and absorption curves, they cut at a pressure 7·4 mm. The sorption velocity is greatest at the commencement, and decreases as the equilibrium conditions are approached; it is also greater at the lower pressures than at the higher pressures. In the case of acetic acid, much the same results are observed, but here an hysteresis occurs. The saturation pressure is greater when reached from above than when reached from below. This is held to be due to the two processes, solution and absorption, occurring simultaneously.   J. F. S.

Electrolytic Conductivity in Non-aqueous Solutions. IV. The Solvation of the Ions of *p*-Tolyltrimethylammonium Iodide in a Number of Organic Solvents. HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1920, [5], **189**, 641—643. (Compare A., 1919, ii, 44).—Walden's formula (this vol., ii, 230) is used to calculate the solvation of the ions of *p*-tolyltrimethylammonium iodide in a number of solvents. The molecular weight of the solute will be increased above the normal value, corresponding with Walden's equation, if solvation occurs. The solvation

values obtained with the solvents were: propaldehyde, 7·73; epichlorohydrin, 3·44; ethyl alcohol, 3·30; methyl alcohol, 2·91; benzaldehyde, 2·88; anisaldehyde, 2·21; propionitrile, 1·44; acetone, 1·29; nitromethane, 0; benzonitrile, 0; nitrobenzene, 0.   Since Walden has shown that the iodide ion is not solvated in methyl alcohol, ethyl alcohol, acetone, and nitrobenzene, the above values probably represent the degrees of solvation of the organic cation. The tendency to solvation in aldehydes decreases with increase in the molecular weights of the latter.   J. R. P.

Tabulation of Hydrogen- and Hydroxyl-ion Concentrations of some Acids and Bases. ARTHUR W. THOMAS (J. Amer. Leather Chem. Assoc., 1920, 15, 133--146).—The hydrogen-ion concentrations of the following acids are given for concentrations from 0·001M to 2M: acetic, boric, butyric, carbonic, citric, formic, gallic, hydrochloric, lactic, nitric, oxalic, phosphoric, salicylic, sulphuric, and tartaric. The hydroxyl-ion concentrations of ammonium, barium, calcium, potassium, and sodium hydroxides are also given. The values for the weak acids were calculated from Ostwald's dilution law, and for the strong acids from curves constructed from data in the literature. CHEMICAL ABSTRACTS.

Surface Energy of Crystals and its Influence on the Crystalline Form. M. BORN and O. STERN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1919, 901—913). A mathematical paper in which the surface energy of a crystal in a vacuum is calculated from the electrostatic forces between the ions.   J. R. P.

Anisotropic Liquids. I. M. BORN (Sitzungsber. Preuss. Akad. Wiss., Berlin, 1916, 614--650). The theory that the molecules of anisotropic liquids are elongated in the direction of one axis, and that the orientations between the axes depend on the temperature, according to a law of distribution, is completed by the calculation of the law of distribution, on the assumption that the molecules are electrical dipoles, and that the directive forces are purely electrical. The liquid crystal is then analogous to the magnet considered in the theory of Langevin and Weiss. The Curie point of a magnet corresponds approximately with the transition point between anisotropic and isotropic states. From the known transition points of anisotropic liquids, the electric moments of the dipoles are calculated. The optical properties of the substances are also calculated, and found in qualitative agreement with experiment. A liquid composed of dipoles will exhibit double refraction in an electric field at sufficiently high temperatures; the expression for Kerr's constant deduced on this theory is similar to that found by Langevin in another manner.   J. R. P.

Anisotropic Liquids. II. Dependence of the Refractive Index at Right Angles to the Optic-axis on the Temperature. M. BORN and F. STUMPF (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1916, 1043—1060). Measurements of the change of refractive

index with temperature made with anisotropic liquids confirm the theory advanced by one of the authors (see previous abstract).

J. R. P.

An Altered Formulation of the Quantum Hypothesis. M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 918—923). _The expression for the energy of a resonator derived from the quantum hypothesis may be obtained on the assumptions that: (1) the exchange of energy between resonators and radiation is continuous, instead of quantum emission and continuous absorption postulated in a previous hypothesis; (2) exchange of energy between resonators and free particles (molecules, ions, and electrons) occurs in quanta. The formulæ of the classical electrodynamics then apply to the reciprocal action between resonators and radiation, and many former difficulties are removed. In the collision of a free particle with a resonator, it is assumed that the latter gives up the whole of its energy to the particle, whilst the particle imparts to the resonator amounts of energy which are whole multiples of the quantum. The free particles in solids may be vapour molecules, since the number required is so small as not to contribute materially to the specific heat of the solid.   J. R. P.

Variance and the means of Presuming its Value without the Aid of any Formula. C. RAVEAU (*Compt. rend.*, 1920, **170**, 1385—1387).—A theoretical discussion of the variance of systems, certain systems being discussed and their variance arrived at without calculation.   W. G.

Equilibrium between Chlorine, Water, Hydrochloric Acid, and Chloric Acid. Free Energy of the Chlorate Ion. AXEL. I. OLSON (*J. Amer. Chem. Soc.*, 1920, **42**, 896—904).—The equilibrium constant of the reaction $3H_2O + 3Cl_2 = HClO_3 - 5HCl$ has been experimentally determined at 91°. The reaction mixture was sealed in glass tubes with a little (0·02M) manganous chloride, which acted as a catalyst. Equilibrium was slowly reached from both sides, and by means of the equation

$$K^1 = (H^+)^6 \times (Cl')^5 \times (ClO_3') / (Cl_2)^3$$

the equilibrium constant is calculated to 10×10^{-6}. The free energy of the reaction $3Cl_2(aq.) - 3H_2O(liq.) - 6H^+ - 5Cl' - ClO_3'$ is 10,600 cal. at 91°, and at 15° it is 6640 cal. The free energy of formation of the chlorate ion is given from the equation $\frac{3}{2}Cl_2(gas) + 1·5O_2 + \ominus - ClO_3'$, for which $\Delta F_{298} - 1374$.

J. F. S.

Registration of Rapid Pressure Changes. W. NERNST (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 896—901).— The behaviour of vibrating membranes used in pressure measurements during gaseous explosions is considered mathematically. The rise of pressure during explosion in a closed vessel is stated to follow the law, $p = p_0(1 - e^{-\alpha t})$, where p_0 is the maximum pressure, t is the time, and α is a constant. The main results, however, are

independent of this special hypothesis. Of the two solutions of the equation, only one has been realised with gaseous explosions, namely, the execution by the registering membrane of vibrations of small amplitude about the position corresponding with the instantaneous pressure. The other solution may be represented by high explosives of the "brisant" type. Great disturbances in the motion of the membrane may occur when wave motion is set up in the gas.   J. R. P.

The Use of Conductometric Titrations in Neutralisation Analysis. I. The Neutralisation of Acids and Bases. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **111**, 1—27).—The object of the experiments was to investigate the relationship between the neutralisation curve on the one hand and the dissociation constants and dilution on the other. The experiments were conducted by titrating a dilute acid solution with a relatively strong solution of the base, so that the dilution of the liquid of which the conductivity was being determined was not appreciably changed during the titration. The neutralisation curve was obtained by plotting the relative conductivities as ordinates against the quantities of alkali added as abscissæ. When a strong acid is neutralised by a strong base, the neutralisation curve falls steeply as a straight line to the neutral point, and then rises steeply as the alkalinity increases. Up to the neutral point, the neutralisation curve is the resultant sum of the acid conductivity curve and the salt conductivity curve. By titrating a solution of the salt into pure water, a curve is obtained, the salt conductivity curve, which cuts the neutralisation curve at the neutral point. The sharpness of the neutral point is independent of the mobility of the anion, but the point becomes less distinct on the neutralisation curve the greater the mobility of the cation.

When an acid of medium strength, such as salicylic acid, is neutralised by a strong base, the neutralisation curve has a concave form and passes through a minimum before the neutral point is reached. Beyond the neutral point, the curve rises sharply as a straight line, but the neutral point is not distinct. It can, however, be found by determining the conductivity curve of the salt, since the salt curve cuts the neutralisation curve in the neutral point. The conductivity of the unneutralised acid at any stage of the neutralisation can be deduced from the neutralisation curve and the salt conductivity curve, or it can be calculated from th ion mobilities. From the "acid depression curve" so obtained, th dissociation constant of the acid can be calculated. To obtain goo titration results at dilutions 0·1, 0·01, 0·001*N*, the dissociation constant of the acid should be less than 5×10^{-4}, 5×10^{-5}, o 5×10^{-6} respectively.

In the titration of a very weak acid with a strong base, the neutralisation curve may, from the start, correspond practically with the salt curve up to the neutral point; if the acid is very weak and the salt highly hydrolysed, it is impossible to determine the neutral point. The dissociation constant of the acid must be

not less than 10^{-10} for a $0.1N$-solution or 10^{-9} for a $0.01N$-solution to obtain good results. Boric acid ($K = 6.6 \times 10^{-10}$) and phenol ($K = 10^{-10}$) were successfully titrated with sodium hydroxide. Weak acids and weak bases can be titrated if their dissociation constants are greater than 3×10^{-6}. Thus acetic acid can be titrated with ammonia, but boric acid cannot, because, on account of the hydrolysis of the neutral salt, the whole neutralisation curve is rounded off, and there is no sharp change of direction at the neutral point.   E. H. R.

The Use of Conductometric Titrations in Neutralisation Analysis. II. The Simultaneous Titration of Different Acids or Bases.

I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, 111, 28—51. Compare preceding abstract).—When a strong and a weak acid are titrated together, the acid conductivity curve falls at first along a straight line. If, when the stronger acid is nearly neutralised, the conductivity of the weaker acid is not negligible, the point of neutralisation of the strong acid is not sharp on the neutralisation curve. It can, however, be found by plotting the conductivity curve of the salt of the strong acid, and finding the point of intersection of this straight line with the first, straight portion of the neutralisation curve. In this way, hydrochloric acid can be titrated, for example, in presence of formic acid. The point of neutralisation of the formic acid is given sharply by the change of direction of the curve when the solution becomes alkaline. To get good results, when titrating $0.1N$-solutions of the two acids in equal concentrations, the dissociation constant of the weaker acid should be less than 4×10^{-4}. Addition of alcohol, which tends to suppress the dissociation of the weak acid, is sometimes advantageous.

Two weak acids can be titrated together in equal concentrations when the ratio of their dissociation constants is smaller than 0.001, but if the concentration of the weaker acid is ten times that of the stronger, the ratio must be smaller than 0.0001. Since, however, the sharpness of the result depends on the magnitude of the angle of intersection of the two straight lines representing the two portions of the neutralisation curve, and the change of direction of the curve depends on the relative mobilities of the anions of the two acids, it follows that the accuracy of the result depends on the mobilities of the anions, and if these are approximately equal, no definite result can be obtained. Thus oxalic acid and tartaric acid, or oxalic acid and phenol, can be titrated together, but not acetic acid and phenol. When a dibasic acid is titrated, the first and second equivalent points can only be found if the two dissociation constants are markedly different. This occurs in the case of oxalic acid. In the case of tartaric acid, the first equivalent point is not sharp even in presence of alcohol, and in the case of succinic acid it cannot be determined at all.

Two weak acids with approximately equal dissociation constants cannot be titrated together, but if the dissociation constants and ion mobilities are known, the composition can be calculated from

the conductivity of the mixture. A fresh determination of the dissociation constant of formic·acid gave $2·05 \times 10^{-4}$ at 18°.

The same considerations apply to the titration of mixtures of bases as to mixtures of acids.   E. H. R.

Catalysis of Oxy-hydrogen Gas by Palladium Mixed Crystals. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **111**, 90—96).—Experiments were made with palladium–silver and palladium–gold alloys, containing from 0 to 100% silver and gold respectively, to determine the influence of the composition of the metal on the temperature at which catalysis of a hydrogen–oxygen mixture (prepared by electrolysis of sodium hydroxide solution) commences and, on cooling, ceases. The observed temperature at which catalysis ceases is generally considerably lower than that at which it commences, because, during cooling, the heat of reaction tends to keep the temperature of the contact surface between catalyst and gas above that of the surroundings. The form of the catalyst also influences the limiting temperatures; for these experiments, the metal was in the form of thin wire wound into a close spiral. With pure palladium, catalysis started at 145—163° and ceased at 35—50°. In the palladium–silver series, both limiting temperatures rose slowly until the proportion of silver reached 80%, when there was a sudden rise to 370—380° (starting temperature) and 270—276° (cessation of catalysis). In the palladium–gold series, there was little change up to 70% gold, then a rapid rise of the limiting temperatures over the range from 70% to 100% gold. There appears to be a close connexion between the velocity of solution of hydrogen in the catalyst and the rate of catalysis. In the palladium–silver series between 200° and 300°, the solubility of hydrogen is very slight in the alloy containing 70–80% silver, and the same is true of the 80% gold alloy in the palladium–gold series. These compositions correspond with the rapid rise observed in the limiting temperature of catalysis. The rate of catalysis probably depends, however, not so much on the actual solubility of hydrogen as on its rate of solution in the catalyst.   E. H. R.

Acceleration of the Decomposition of Hydrogen Peroxide by Colloidal Rhodium. C. ZENGHELIS and B. PAPACONSTANTINOS (*Compt. rend.*, 1920, **170**, 1178—1180. Compare this vol., ii, 380).—The decomposition of hydrogen peroxide by a colloidal solution of rhodium is a unimolecular reaction, the velocity of which is considerably accelerated by previously bubbling either hydrogen or carbon monoxide through the colloidal solution.
                                W. G.

Catalytic Actions at Solid Surfaces. III. Hydrogenation of Acetaldehyde and the Dehydrogenation of Ethyl Alcohol in the Presence of Finely Divided Metals. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [A], **97**, 259—264. Compare A., 1919, ii, 403; this vol., ii, 102).—The hydrogenation of acetaldehyde and the dehydrogenation of ethyl alcohol in the presence of metallic nickel and copper have been investigated at

temperatures 120—300°. It is shown that acetaldehyde is converted into ethyl alcohol by hydrogen under these conditions, in the case of copper at 200° the yield of alcohol being 87·6%; in the case of nickel, the aldehyde has a tendency to break up into carbon monoxide and methane. In the dehydrogenation of alcohol in the presence of copper, a yield of 90—95% of acetaldehyde may be obtained at 295—300°. In the dehydrogenation of alcohol, the presence of water improves the yield of acetaldehyde relatively to that of hydrogen. There are always small quantities of by-products, notably n-butaldehyde, crotonaldehyde, and ethyl acetate, the total amount of which is normally 1—2%. The presence of a small proportion of water protects acetaldehyde from hydrogenation, and in some cases prevents the action entirely. The primary action of the catalyst in all these cases is to effect an association with the carbon compound, the resulting unstable complex then being resolved into other compounds.   J. F. S.

Catalytic Actions at Solid Surfaces. IV. Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 265--273. Compare preceding abstract). The reaction $CO + H_2O \rightleftharpoons CO_2 + H_2 + 10{,}200$ cal. has been studied, using both ferric oxide and copper as contact substances. The reaction has been carried out using 95% carbon monoxide and using water-gas containing 40% carbon monoxide at temperatures from 227° to 600°. It is shown that copper is much less complete in its action than iron oxide at the higher temperatures, but over the range 200—300° it is definitely more active than iron oxide. Copper commences to act at a reasonable rate at about 220°, whereas iron oxide is barely active at 250°, and does not reach full activity until about 400°. On passing water-gas (5·1% carbon dioxide, 39·9% carbon monoxide, and 47·3% hydrogen) with steam in the presence of ammonia through a tube at 350°, sufficient ammonium formate was obtained for purposes of identification. The relative activities of copper and iron oxide toward carbon monoxide and steam at the lower ranges of temperature are closely parallel to their respective powers of decomposing formic acid and steam. The amount of action effected by the copper catalyst declines somewhat after 350°, and the maximum change effected appears to be greater the higher the proportion of carbon monoxide in the gas.   J. F. S.

Heat of Dissociation of Hydrogen according to the Bohr-Debye Atom Model. M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 914--931). The heat of dissociation of a hydrogen molecule is, at sufficiently low temperatures, equal to the difference between the energy of the two atoms and that of the molecule. On the first assumption, that in all the atoms and all the molecules of hydrogen the electrons describe circular orbits with single quanta, the heat of dissociation is found to be 62,100 cal. The actual value is higher, probably in the region of

100,000 cal.   On the second assumption, that in all the atoms and all the molecules those electronic orbits which possess less than one quantum are correspondingly probable, the heat of dissociation is found by classical mechanics to be infinite; on the theory of relativity it would be 570,000 cal., which is certainly too high. The value 140,000 cal., in much better agreement, is obtained on the assumption that, in addition to circular orbits, the electrons may perform pendulum oscillations.   It is concluded that the arbitrary assumption of circular orbits made by Bohr is not justified.   J. R. P.

The Absolute Calculation of Crystal Properties from Bohr's Model Atom. M. BORN and A. LANDÉ (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 1048—1068).—A mathematical paper in which the positions of the atoms in a cubic space-lattice are deduced from Bohr's model of the atom.   J. R. P.

Metals. I. and II. F. HABER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 506—518. 990—1007).—I. The elastic properties and photoelectric effect are discussed on the hypothesis that a metal consists of a space-lattice of positive ions and free electrons. II. The energies of salts, heats of hydration of ions, the Volta effect, etc., are calculated.   J. R. P.

Apparatus for Measuring [and Circulating] Gases Soluble in Water. BERNHARD NEUMANN and HEINRICH SCHNEIDER (*Zeitsch. angew. Chem.*, 1920, **33**, 128).—An apparatus suitable for measuring and circulating small quantities of gas, soluble in water, consists essentially of two pipette-shaped glass vessels, A and B, provided at the upper ends with T-pieces having stop-cocks, 1, 2, 3, 4, and terminating below in stop-cocks, 5, 6, the latter being connected by a T-piece, C, and in communication with a levelling vessel, D.   The top T-pieces are connected by another T-piece, E, as well as by a bent tube, H, with a lateral branch, J, provided with a stopcock, 8, and leading to the gas reaction vessel or other apparatus.   E is connected by tubing to a gas collector, F, with a three-way tap, 9, and G is a pressure vessel for controlling the movement of gas in F.
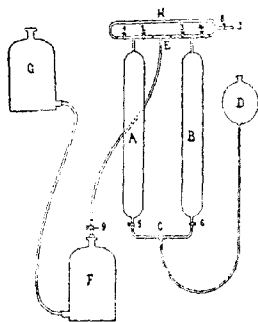
A and B are first half filled with water saturated with the gas.   By suitable manipulation of the stopcocks, gas is introduced into A, and the air is expelled through B, after which gas is introduced into B, the whole apparatus now being filled with gas, and further solution by the

water being prevented. The gas may be circulated through both vessels or retained in either for measurement under atmospheric pressure.　　　　　　　　　　　　　　　　W. J. W.

Inorganic Chemistry.

Improved Kipp's Apparatus for the Preparation of Chemically Pure Hydrogen in the Laboratory. M. DOLCH (*Chem. Zeit.*, 1920, **44**, 378).—The gas delivery tube from the central bulb of a Kipp's apparatus is connected by a three-way cock and side-tube to a stopper and three-way cock in the mouth of the top globe, which is also connected through a second tube to a mercury trap. Pure stick zinc is used in the central bulb, and the apparatus is filled with pure hydrogen before the introduction of air-free dilute sulphuric acid. The space above the acid in the top bulb, being connected to the generator bulb, is always filled with hydrogen, which can be drawn off at will from either bulb by suitably placing the three-way cocks. Excess of pressure is released through the mercury trap.　　　　　　　　E. H. R.

Triatomic Hydrogen. GERALD L. WENDT and ROBERT S. LANDAUER (*J. Amer. Chem. Soc.*, 1920. **42**. 930—945).—A reactive modification of hydrogen has been produced by several methods, all of which are dependent on gaseous ionisation: (i) by the α-rays from radium emanation, (ii) by an electrical discharge under reduced pressure, and (iii) by the high potential corona at atmospheric pressure. Attempts to produce activation by Schumann light rays failed. This active hydrogen reduces sulphur, arsenic, phosphorus, mercury, nitrogen, and both acid and alkaline solutions of potassium permanganate. It is condensed or destroyed by temperatures about that of liquid air. It is very unstable, and reverts to the ordinary form in about a minute. It passes readily through glass wool, and is not less stable at atmospheric pressure than at low pressures. The activity is not due to gaseous ions, and the properties of the gas are quite different from those of Langmuir's atomic hydrogen (A., 1912, ii, 826, 1162; 1914, ii, 104; 1915, ii, 249). The formation of a polyatomic molecule is indicated by the contraction of the hydrogen when ionised. Positive ray analysis at very low pressures shows a large proportion of triatomic molecules, which are undoubtedly the molecules responsible for the chemical activity. All the properties of the gas point to it being an ozone form, perhaps, properly called "*hyzone.*" The existence of triatomic hydrogen is applied to the explanation of Lind's "cluster ion" hypothesis (A., 1912, ii, 513). The calculations of Bohr, based on the Rutherford atom, furnish the only valency hypothesis which satisfactorily accounts for the existence of triatomic hydrogen.　　　　　　　　　　　J. F. S.

Chemical Decomposition of Hydrogen Peroxide. CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 1, 1—18; from *Chem. Zentr.*, 1920, i, 723).—The author confirms Kistiakowsky's observation that the decomposition of hydrogen peroxide in light is notably catalysed by the presence of potassium ferrocyanide. When dilute mixed solutions are placed in ultra-violet light, decomposition ensues very slowly at first, subsequently more rapidly, and finally attains a constant rate; the phenomenon is explained by the assumption of the gradual formation of an extremely stable substance which catalytically accelerates the decomposition of hydrogen peroxide.   H. W.

The Behaviour of Non-metallic Hydrides towards Chlorine. ALFRED STOCK [with ROBERT WINTGEN] (*Ber.*, 1920, **53**, [*B*], 837—842).— The experiments recorded in the literature of this subject are concerned for the most part with the products obtained by rather drastic action. The author gives an extended review of the available data, and describes a series of experiments, some of them of a preliminary nature, on the regulated action of the halogen, the experiments being performed at low temperature and frequently in the presence of an inert solvent, such as liquid hydrogen chloride. In spite of certain gaps in the evidence, the following statements may be made. Only five non-metals yield partly chlorinated hydrides which are stable at the ordinary temperature, B_2H_5Cl, CH_3Cl, SiH_3Cl, CH_2Cl_2, SiH_2Cl_2, $CHCl_3$, $SiHCl_3$, NH_2Cl, ($NHCl_2$?), $OHCl$. Amongst these, the compounds of boron, nitrogen, and oxygen are most unstable, whilst chloromonosilane is more readily decomposed than methyl chloride, a close dependence on the position of the element in the periodic system being observable. The maximum stability is observed with carbon, and is attributable to the equality in the affinity of this element for positive and negative groups. The stability of the partly chlorinated hydrides diminishes in all directions from carbon. The compounds exhibit a more or less strongly marked tendency to decompose into the pure hydride and pure chloride (for example, B_2H_5Cl into B_2H_6 and BCl_3). In the nitrogen group (N,P,As,Sb), in which the instability of the partly chlorinated hydride increases with increasing atomic weight of the nuclear element, reaction immediately occurs, either with the initial hydride or by further action of the initial decomposition products among themselves, whereby hydrogen chloride is eliminated, and either condensed hydrides relatively poorer in hydrogen (N_2H_4,P_2H_4; that is, $NH_2Cl + NH_3 = N_2H_4 + HCl$) or the free elements (that is, $AsCl_3 + AsH_3 = 2As + 3HCl$) are formed. The former frequently are further converted into solid hydrides still poorer in hydrogen ($P_{12}H_6,P_9H_3,AsH[?]$). In the oxygen group, the ability to form a partly chlorinated hydride is only observed in the element of smallest atomic weight, oxygen itself ($OHCl$). In this compound, the tendency towards decomposition into hydride and chloride is still observable ($2OHCl = OH_2 + OCl_2$), but the change to hydrogen

hloride and oxygen is more characteristic. Correspondingly, the ction of chlorine on the remaining hydrides of the oxygen group rads exclusively to the formation of the free elements, S, Se, Te.

H. W.

Electrolysis of Hydrogen Bromide in Liquid Sulphur Dioxide. LANCELOT SALISBURY BAGSTER and GEORGE COOLING (*T.*, 1920, **117**, 693—696).

Bromine Chloride: its Combination with Ethylene. MARCEL DELÉPINE and LUCIEN VILLE (*Compt. rend.*, 1920, **170**, 1390—1392).—Although physical chemists deny the existence of a bromine chloride, the authors consider that the behaviour of a solution of chlorine in bromine towards ethylene, the main product being chlorobromoethane, is strong evidence in favour of the existence of such a compound.   W. G.

The Photochemical Oxidation of Hydrogen Iodide. CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 2, 1–28; from *Chem. Zentr.*, 1920, i, 723–724).—Thin, rapidly moved layers of hydrogen iodide solution, when subjected to the conjoint action of oxygen at a constant pressure and light, are oxidised very slowly initially, then more rapidly until the process attains a constant velocity. The phenomenon is due to the auto-sensitising action of the liberated iodine. Similar action is observed in the cases of the photochemical oxidation of the leuco-bases of certain dyes (Gros, 1901), of alkaline solutions of pyrogallol (Trautz and Thomas, 1908), and of aqueous sodium sulphite solution (Trautz, 1909). In each instance, a slow oxidation at any rate must be assumed to occur in the dark.   H. W.

The Estimation of the Density of Oxygen according to Dewar and Kamerlingh Onnes. RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1920, **12**, 14; from *Chem. Zentr.*, 1920, i, 661).—The data obtained by Dewar in 1902 and by Onnes in 1911 for the vapour density of oxygen are in good agreement at −182° with Gay-Lussac's law although the latter is known not to hold at such low temperatures. The author now shows that the values for the apparent alteration in volume are in accordance with the law, but that such values are not in reality the data which are to be determined; after applying the necessary corrections, much lower results are obtained.   H. W.

Rutherford's Experiments on the Subdivision of the Nitrogen Nucleus. W. LENZ (*Naturwiss.*, 1920, **8**, 181—186; from *Chem. Zentr.*, 1920, i, 768). The theory of relativity, according to which mass is connected with every energy, throws light on the questions of simple numbers for atomic weights and of the stability of nuclei. From this point of view, the stability of the helium nucleus is readily understood, whilst the instability of the nitrogen nucleus is explicable. The author considers the persistent oxygen radiations to be possibly helium α-rays.   H. W.

Action of Nitrous Acid on Coloured Indicators. O. MATIGNON and G. GIRE (*Bull. Soc. chim.*, 1920, [iv], **27**, 362—366). —A mixture of nitric and nitrous acids was titrated with $N/10$ sodium hydroxide, different indicators being used for the different titrations. Of the indicators used, only sodium ferric salicylate characterised the nitrous acid, and this was not sharp. Thus nitrous acid, contrary to the conclusions derived from the heats of neutralisation, is a much stronger acid than the second acid function of phosphoric acid. This is borne out by a study, by electrical conductivity measurements, of the progressive displacement of nitrous acid by sulphuric acid in a dilute solution of sodium nitrite.

W. G.

Production of Concentrated Nitric Acid from Nitrous Gases. F. FOERSTER, TH. BURCHARDT, and E. FRICKE (*Zeitsch. angew. Chem.*, 1920, **33**, 113—117, 122—127, 129—132).—The concentration of nitric acid above 68—69%, by treatment of dilute nitric acid with nitrogen peroxide, water, and oxygen, may be effected if the time of treatment is extended, the oxygen used only in slight excess, and the gas velocity reduced. Even so, only 80% nitric acid is produced. A very high concentration results by interaction of the weak nitric acid solution with sufficient excess of liquid nitrogen peroxide, followed by slight agitation with oxygen. When the equilibrium $2NO_2 \rightleftharpoons N_2O_4$ is reached in the treatment of nitrous gases with water, nitric peroxide dissolves, and thereby initiates the interaction $N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2$, the nitrous acid being then decomposed into nitric acid and nitric oxide, and oxidised.

W. J. W.

Red Phosphorus as a Reducing Agent. LUDWIG ROSENSTEIN (*J. Amer. Chem. Soc.*, 1920, **42**, 883—888).—The reactions between red phosphorus and acid solutions of a number of salts have been investigated, and a possible application of this substance as a reagent in qualitative analysis has been indicated. The experiments were effected by boiling the solution with 200 mg. of red phosphorus for a few minutes. Silver salts yield an insoluble phosphide, mercuric and mercurous salts are reduced to the metal, palladium and osmium salts are reduced either to the metal or a phosphide, gold salts are converted into an insoluble phosphide, stannic salts are partly reduced to stannous salts, ferric salts are reduced to ferrous salts, iridic salts to iridous, selenates are reduced to the element or to an insoluble phosphide, molybdates are reduced to quadrivalent molybdenum salts, vanadates are reduced to tervalent vanadium salts, dichromates to chromic salts, and permanganates to manganous salts. Bismuth, lead, cadmium, antimony, and arsenic salts, arsenates and stannous salts, are not reduced by red phosphorus. Tellurates and platinichlorides are reduced very slowly by red phosphorus.

J. F. S.

Carbon Formed in the Reaction between Calcium Carbide and Nitrogen. A. REMELÉ and B. RASSOW (*Zeitsch. angew. Chem.*, 1920, **33**, 139—140).—On decomposing calcium cyanamide

(obtained by the interaction of calcium carbide and nitrogen) with water at 160—180° to produce ammonia, the products of the decomposition included small quantities of carbon. This was freed from the bulk of calcium carbonate by treatment with hydrochloric acid, and was purified by fusion with potassium hydroxide or treatment with hydrofluoric acid. It was thus left as graphitic carbon containing 98·15 to 99·4% C, 0·13 to 1·64% H, and 0·43 to 1·48% of residue. It had $D^{15·5}$ 2·250, ignited at 600—640°, and closely resembled Acheson graphite in its electrical conductivity. When oxidised, it yielded a graphitic acid containing 54·81% C, 1·79% H, and 43·40% O, and showing only very slight colloidal properties. When fused with potassium hydroxide, it reacted (like Acheson graphite) at 500°, with the evolution of hydrogen, whereas Ceylon graphite yielded scarcely any gas at 750°. It was not attacked by strong nitric acid.   C. A. M.

**Charcoal before the War. II.** WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 201—224. Compare this vol., ii, 309). —A general discussion on charcoal, in which the removal of inorganic matter, such as calcium carbonate and calcium sulphate, from charcoal which has been used in sugar refining is discussed. The decolorising power of bone-black and methods of preparing synthetic bone-black are considered.   J. F. S.

Silicon Hydrides. VIII. Halogen Derivatives of Disilane and their Hydrolysis. ALFRED STOCK and KARL SOMIESKI (*Ber.*, 1920, **53**, [*B*], 759—769. Compare A., 1916, ii, 319; 1918, 110, 111; this vol., ii, 31).—The behaviour of disilane, Si_2H_6, towards halogen acids has been investigated, and is found to resemble closely that of monosilane.

Disilane does not appear to react with hydrogen chloride at the ordinary temperature or at 120°; in the presence of a little sublimed aluminium chloride, however, reaction occurs more or less readily, according to the general scheme

$$Si_2H_6 + xHCl = Si_2H_{6-x}Cl_x + xH_2,$$
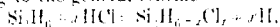
and the course can be followed readily by condensation, by liquid air, of all the components, except hydrogen, and measurement of the volume of the latter. The activity of the aluminium chloride appears to vary considerably with different preparations, and a satisfactory explanation of this behaviour is not at present forthcoming. A mixture of chlorides is invariably produced, the equilibrium lying in favour of the intermediate members of the series. Thus with hydrogen chloride (1 vol.) and disilane (less than 1 vol.), the main product is *dichlorodisilane*, very little *monochlorodisilane* being obtained; with the gases in the volume ratio 2:1, much *trichlorodisilane*, in addition to dichlorodisilane, is produced. Complete chlorination is not, however, effected by a large excess of hydrogen chloride. By reason of the small amount produced, it has not been found possible to isolate monochlorodisilane in the pure state. The final purification of dichlorodisilane could also

not be effected, since it forms a mixture of constant boiling point with trichlorodisilane. The experiments, however, indicate that, as in the case of the carbon compounds, mixtures of isomerides are formed in the halogenation of disilane.

The bromination of disilane has been studied in a precisely analogous manner, and *monobromodisilane*, m. p. $-100°$ to $-101°$, has been isolated in a state of purity. As in the case of the chlorination, the tendency towards the formation of higher derivatives is very pronounced; for instance, in the action of equal volumes of hydrogen bromide and disilane, less than one-third of that portion of the latter which undergoes reaction is converted into the monobromo-derivative.

The hydrolysis of the halogenated disilanes corresponds exactly with that of the similar monosilanes. Thus monobromodisilane readily reacts with water to yield the *substance*, $(Si_2H_5)_2O$, colourless liquid, which can be volatilised without decomposition, and, when dissolved in benzene, instantaneously reduces cold silver nitrate, but not copper sulphate, solution. It reacts slowly but quantitatively with sodium hydroxide solution in accordance with the equation $(Si_2H_5)_2O + 8NaOH + 3H_2O = 4Na_2SiO_3 + 12H_2$. The solid products obtained by the hydrolysis of dibromodisilane and more highly halogenated derivatives closely resemble silico-oxalic acid, $(HO_2Si \cdot SiO_2H)_x$. They are only slowly hydrolysed further by water, can be dried in a desiccator without marked decomposition, are blackened by silver nitrate solution, owing to the deposition of metallic silver, evolve hydrogen when treated with alkali hydroxide, and finally yield a residue of silicate, and explode feebly when heated on platinum foil, evolving gas and becoming discoloured. Evidently the Si–Si linking remains intact in them. This bond appears to be more stable towards alkali than would be expected from earlier statements. Thus two stages can be clearly distinguished in the action of alkali on $(Si_2H_4O)_x$, namely, a violent evolution of gas with accompanying solution of the substance, and then a much slower, persistent change, which can speedily be brought to an end by warming the solution. The first phase corresponds with the hydrolytic separation of the hydrogen atoms, $(Si_2H_4O)_x + 3H_2O = (HO_2Si \cdot SiO_2H)_x + 4H_2O$, whilst the second is due to the gradual conversion of sodium silico-oxalate into sodium silicate and hydrogen.   H. W.

Prolonged Action of Carbonic Acid on Silicates and Quartz.

C. MATIGNON and (Mlle) MARCHAL (*Compt. rend.*, 1920, **170**, 1184–1186).– Quartz, wollastonite, dioptase, mica, talc asbestos, and glass, respectively, in aqueous suspension were submitted to the action of carbon dioxide under 10 atmos. pressure for ten years and three months. At the end of this time, all the silicates and the quartz itself were more or less corroded, and varying amounts of silica had passed into solution. Wollastonite showed the greatest signs of attack and the glass the least.   W. G.

Action of Alcohol on the Sulphates of Sodium. GERALD SNOWDEN BUTLER and HORACE BARRATT DUNNICLIFF (T., 1920, 117, 649—667).

Search for an Alkali Element of Higher Atomic Weight than Cæsium. L. M. DENNIS and R. W. G. WYCKOFF (J. Amer. Chem. Soc., 1920, 42, 985—990).—The alkalis from 3500 grams of pollucite, which contains more than 30% of cæsium oxide, have been examined to see if they contain the next higher homologue of cæsium. The mineral was decomposed by boiling with hydrochloric acid, and, after dilution, filtered. The filtrate was treated with ammonia and ammonium carbonate, whereby a precipitate, consisting mainly of aluminium hydroxide, was obtained. To guard against possible loss of ekacæsium at this point, the aluminium hydroxide was dissolved in sulphuric acid, and the alums thus formed were recrystallised until the ammonium alum had been eliminated. The residual alums were added to those obtained later and treated as described below.

The filtrate from the aluminium hydroxide was evaporated and the residue converted into chlorides, of which 1250 grams were obtained. These were submitted to a series of fractional crystallisations and precipitations with hydrogen chloride. The most soluble fraction, which, according to the order of the solubilities of the alkali chlorides, would contain ekacæsium chloride, was converted into perchlorates, which were fractionally dissolved until the least soluble fraction had been reduced to 10 grams. The end fractions all showed the presence of cæsium alone, and no fraction indicated the presence of ekacæsium when the arc spectrum was examined. The majority of the chlorides were converted into sulphates and fractionated until only 200 c.c. of the saturated solution remained; this, on examination by the arc spectrum, contained only cæsium. The last fraction of the sulphate crystallisation was converted into the alums, and these fractionated, but in no fraction was there any indication of ekacæsium. [See also Richards and Archibald, A., 1903, ii, 366; Baxter, A., 1915, ii, 97.]
                                                              J. F. S.

Melting Point of Normal Ammonium Sulphate. CARL CASPAR (Ber., 1920, 53. [B], 821).—When heated in an open tube, normal ammonium sulphate softens at about 310°, melts at 335°–339°, and decomposes, with evolution of gas, at 355°; in a closed tube it softens from about 360°, and has m. p. 417 –423°. The datum, 140°, recorded in the literature is based on a misapprehension, and refers in reality to ammonium hydrogen sulphate.
                                                              H. W.

Solubility of Mono- and Di ammonium Phosphate. G. H. BUCHANAN and G. B. WINNER (J. Ind. Eng. Chem., 1920, 12, 448–451).—The solubility (grams in 100 grams of the saturated solution) of monoammonium phosphate between 5° and 90° is 30·0–0·455t; that of diammonium phosphate between 10° and 70° is 36·5–0·213t.
                                                              W. P. S.

Mixed Colloids of Calcium Fluoride. A. MAZZUCCHELLI and D. VITA (*Gazzetta*, 1920, **50**, i, 232—245. See Paternò and Mazzucchelli, A., 1904, ii, 169).—Colloidal calcium fluoride, prepared by pouring potassium fluoride solution into excess of calcium chloride solution, possesses a negative charge, this observation being in accord with the behaviour noted by Lottermoser with silver salts, which in the colloidal state exhibit the sign of the ion in excess at the moment of their formation (A., 1905, ii, 586). Mixed colloidal solutions containing calcium fluoride and another insoluble salt have been prepared by mixing solutions of suitable salts. Moderately stable mixed colloidal solutions are formed by calcium fluoride with $Ca_3(PO_4)_2$, $AgCl$, $AgBr$, AgI, Ag_3PO_4, Ag_2S, CuS, $Fe(OH)_3$, and $Si(OH)_4$, the last of these being thus obtained in the colloidal condition in a solution neutral to methyl-orange. Less stable colloidal solutions, obtainable only under certain conditions, are formed with $CaCO_3$, CaC_2O_4, $AgCNS$, Ag_2CrO_4, Ag_2MoO_4, ZnS, CdS, MnS, $PbCrO_4$, $PbSO_4$ (very slightly stable), and $BaSO_4$. With As_2S_3, immediate precipitation occurs.

T. H. P.

Slaked Lime and Milk of Lime. BERNHARD KOSMANN (*Zeitsch. Elektrochem.*, 1920, **26**, 173—181).—Polemical: a long discussion on the processes occurring in the slaking of lime, in which the views of Kohlschütter and Walther (A., 1919, ii, 342) are criticised. The author is of the opinion that the slaking of lime consists in a gradual step-wise combination with water, in which the following substances are produced in order: $Ca(OH)_2$, $HCa(OH)_3$, $H_2Ca(OH)_4$, $H_3Ca(OH)_5$, $H_4Ca(OH)_6$, $H_5Ca(OH)_7$, $H_6Ca(OH)_8$, and $H_7Ca(OH)_9$.

J. F. S.

[Slaked Lime and Milk of Lime.] V. KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1920, **26**, 181—182).—An answer to Kosmann (preceding abstract).

J. F. S.

An Unusual Deposit of Aragonite from Sea Water. ROGER C. WELLS (*J. Washington Acad. Sci.*, 1920, **10**, 249—254).—Small crystals of aragonite were found on the walls of a sealed glass tube which had contained sea-water for several years. The most probable explanation of the formation of the deposit is that alkali had been slowly dissolved from the glass, causing partial conversion of calcium hydrogen carbonate into carbonate. The solubility product $[Ca^{++}][CO_3^{--}]$ for the sea-water under consideration is calculated to be 7.2×10^{-10} at $25°$.

E. H. R.

### Reactions between Primary Potassium Phosphate and Increasing Quantities of Calcium Hydrogen Carbonate during Boiling. W. WINDISCH and W. DIETRICH (*Woch. Brau.*, 1920, **37**, 177—180, 187—189).—The precipitates obtained by boiling solutions of primary potassium phosphate with increasing proportions of calcium hydrogen carbonate show increasing percentages of calcium, which range from that corresponding with

secondary to that corresponding with tertiary calcium phosphate. The precipitates appear to entrain soluble alkaline compounds, since the alkalinities of the filtrates (due to formation of secondary potassium phosphate) are lower than the calculated values.

L. E.

A Sulphato-chromate Regarded as an Individual Substance. A. DUFFOUR (*Bull. Soc. franç. Min.*, 1919, **42**, 247; from *Chem. Zentr.*, 1920, i, 726).—The author has vainly endeavoured to repeat the preparation of potassium magnesium sulphato-chromate, $2MgSO_4,K_2CrO_4,9H_2O$, described by Etard (this Journ., 1877, ii, 847). Crystals similar to those obtained by the latter separate from a solution containing magnesium sulphate (2 mols.) and potassium chromate (1 mol.), but these are assigned by the crystallographical properties to the series of isomorphous magnesium double sulphates, which they also resemble chemically in losing two-thirds of their water of crystallisation at 120°. A case of mixed crystals of the general composition

$$n[K_2Mg(SO_4)_2,6H_2O] + (100 - n)[K_2Mg(CrO_4)_2,6H_2O]$$
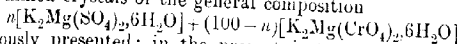
is obviously presented; in the present instance, $n = 84.5$, whereas with Etard's preparation, the analyses of which were confined to the estimation of CrO_3 and of the loss at 250°, the value of n was 64.5. The loss in weight at 250°, however, exceeds the weight of water, since magnesium chromate begins to decompose, with evolution of oxygen, at this temperature. From a solution of a molar mixture of sulphate and chromate, the former separates first isomorphously mixed with 5.5 mols.% of the latter; after separation of the excess of potassium salts, the first mixed crystals of potassium magnesium sulphato-chromate have $n = 72.4$. From solutions richer in chromate, for example, from such as contain three times as much double chromate as double sulphate, the double salt immediately separates in triclinic crystals ($+ 2H_2O$). When, however, the solution is allowed to evaporate at 20°, with careful exclusion of any seed of the triclinic salt, a monoclinic *heptahydrate* may be obtained in small amount, the composition of which approximates to that of the mother liquor. The compound is, however, metastable, and, after a few days, shows efflorescent patches of the triclinic dihydrate, into which it is slowly transformed.

H. W.

Crystalline Structure of Zinc Oxide. W. LAWRENCE BRAGG (*Phil. Mag.*, 1920, [vi], **39**, 647–651).—The crystalline structure of zinc oxide has been determined by measurement of the X-ray spectrum. It is shown that the zinc atoms are arranged on two hexagonal space-lattices, their centres corresponding very closely with those of a set of equal spheres in hexagonal close packing. In the latter case, the axial ratio is $a : c = 1 : 1.632$, whilst that for zinc oxide is $a : c = 1 : 1.608$. The positions of the zinc atoms are identical with those of the hexagonal close-packed arrangement of spheres, if the latter be supposed to contract in the direction parallel to the hexagonal axis, so as to reduce the ratio $c : a$ from

1·632 to 1·608. The oxygen atoms are probably on two hexagonal space-lattices identical with those on which the zinc atoms are situated, and derived from the latter by a movement of translation parallel to the c axis, which brings every oxygen atom into the centre of four zinc atoms arranged at the corners of what is very nearly a regular tetrahedron. The observed spacings agree well with the calculated values; they are: plane (0001), $c/2 = 2\cdot58$ A.U.; (10$\bar{1}$0), $a\sqrt{3}/2 = 2\cdot80$ A.U.; (11$2$0), $a/2 = 1\cdot61$ A.U.; (10$\bar{1}$1), $2\cdot47$ A.U.   J. F. S.

Atomic Weight of Lead from a Japanese Radioactive Mineral.

THEODORE W. RICHARDS and JITSUSABURO SAMESHIMA (*J. Amer. Chem. Soc.*, 1920, **42**, 928—930).—Lead obtained from a mineral crust found at the bottom of a hot spring in Hokuto, Formosa, Japan, has been used for atomic weight determinations. This mineral, according to Hayakawa and Nakano (A., 1912, ii, 1123), contains also cerium, barium, lanthanum, ionium, polonium, and radium, but no uranium or radio-lead. The metallic lead was converted into the chloride, and the ratio $PbCl_2 : 2Ag$ determined by Richards's method (A., 1914, ii, 653), when, as the mean of three determinations, the value 207·13 was obtained for the atomic weight. This indicates that the material is mainly ordinary lead, with possibly 5% of an isotope of lower atomic weight.   J. F. S.

The Separation of the Rare Earths by Basic Precipitation.

I. WILHELM PRANDTL and JOHANNA RAUCHENBERGER (*Ber.*, 1920, **53**, [*B*], 843—853).—In its usual form the basic process for the separation of the rare earths suffers from the drawback that the solubility of the precipitated hydroxides or basic salts in the mother liquor is, in general, very small, and the absolute difference in solubility between the hydroxides of neighbouring earths is minimal; in order, therefore, to avoid local excesses of hydroxyl ions and to achieve a reasonably successful fractionation, it is necessary to work with exceedingly dilute solutions which necessitate lengthy evaporations, etc. An amended process is now proposed which permits the use of solutions of any concentration, it being only necessary to ensure that precipitation is sufficiently slow to be truly selective, and that the most sparingly soluble substance actually separates. This can be effected more advantageously by increasing the solubility of the precipitate in the mother liquor than by simple dilution, whilst at the same time the absolute differences in solubility between the precipitates of neighbouring earths is increased and their precipitation is delayed. Since the reaction between ammonia and the salts of the alkaline earths is reversible, $MCl_3 + 3NH_4\cdot OH \rightleftharpoons M(OH)_3 + 3NH_4Cl$, its course is dependent on the concentration of the ammonium salt; increase in the concentration of the latter increases the solubility of the earth hydroxide in the mother liquor within certain limits, and delays its precipitation by ammonia.

The authors have attempted to measure the equilibrium of the reaction under varying conditions in the cases of lanthanum, neodymium, and praseodymium, and have obtained similar, but not identical, results by approaching the subject from the two sides. Since it is found that the precipitate does not consist of the pure hydroxide, but of a strongly basic chloride of varying composition, the pure oxides were treated at the requisite temperature with ammonium chloride solution on the one hand and the basic chlorides so formed were subjected to the action of 1, 2, 3, 4, and $5N$-ammonium chloride solution, whilst, on the other hand, the metallic chlorides were treated with the equivalent quantity of ammonia and so much ammonium chloride as to make 1, 2, 3, 4, and $5N$-solutions of the latter at $15°$, $30°$, $50°$, and $100°$ in closed vessels until equilibrium was established, after which the amount of ammonia and of earth in the solution were estimated. It is found that the solubility of the basic salts (formed from the oxides) in ammonium chloride solution is always less than that of the basic salts obtained by precipitation with ammonia. In either case, the solubility of the precipitates increases to a maximum with $3N$-ammonium chloride solution, and then diminishes. It is also observed that under otherwise similar conditions, the content of the solution in earthy metal, but not that of ammonia, to a marked extent depends on the amount of the precipitate, which indicates an adsorption of the (partly colloidally) dissolved earthy salt by the precipitate. The curves also show that lanthanum is relatively greatly distinguished from the didymium component by its greater basicity, and that neodymium and praseodymium are very similar in this respect. They also indicate an extremely important influence of temperature on the separation process; the lanthanum curves for 2 and $3N$-ammonium chloride solution are so widely separated from the didymium curves at $50°$ that a separation should be readily possible, whilst, on the other hand, at a slightly higher temperature, but still under $100°$, the curves intersect, so that a separation is then impossible. The praseodymium and neodymium curves generally lie very close together and intersect at definite temperatures. The approximation of the curves at higher temperatures is probably explained by the more complete conversion of the precipitate into the hydroxides, the absolute differences between the solubilities of which are very slight.

Basing their procedure on the experiments just detailed, the authors describe a very successful method for the separation of lanthanum from its mixtures with much didymium. The impure oxide is dissolved to a nearly neutral solution in moderately concentrated hydrochloric acid, an amount of ammonium chloride equal to the weight of the oxide is added, and sufficient water to make the solution 2—$3N$ with respect to ammonium chloride. The solution is heated to $50°$ in a capacious porcelain dish, and a mixture of equal volumes of $4N$-ammonia and $4N$-ammonium chloride solutions is slowly added with vigorous stirring. As soon as a moderate amount of precipitate has been formed (about 5% of the

original oxide) the operation is interrupted, the precipitate is removed, and a second precipitation is effected in the clear filtrate. The alternate precipitation and filtration are repeated in this manner until the filtrate no longer exhibits absorption lines.

H. W.

The Action of Concentrated Sulphuric Acid on Iron. III.
CHARLES E. FAWSITT (*J. Soc. Chem. Ind.*, 1920, **39**, 147—148T. Compare A., 1914, ii, 274).—Experiments on the effect of concentrated sulphuric acid of different strengths on a steel containing C, 0·51%; P, 0·046%; Si, 0·083%; S, 0·058%; and Mn, 0·48%, showed that the velocity of attack increased as the acid was diluted from 97% to 90·9% H_2SO_4; it appeared then to drop suddenly at 89·3%, and below 85% increased rapidly. Shaking has an important effect in increasing the velocity of action. Steel which has been made passive by immersion in nitric acid will sometimes resist the action of concentrated sulphuric acid, but at times the treatment fails to afford protection. In some instances partial immersion of a piece of steel in nitric acid has caused the whole piece to resist the action of sulphuric acid. The addition of nitric acid or a nitrate to the sulphuric acid, however, intensifies its action on steel. The effect of the addition of a number of substances to the sulphuric acid was investigated, including potassium persulphate, sodium sulphate, sodium hyposulphite, and arsenious acid, but none of these had any appreciable protective action.   E. H. R.

The Nickel Plating of Aluminium and its Alloys. LÉON
GUILLET and MAXIME GASNIER (*Compt. rend.*, 1920, **170**, 1253—1256). The surface of the aluminium is first prepared by subjecting it to a sand blast. The sand should be capable of passing through a 0·2 mm. sieve, and be used under a pressure of 1500 grams cm.^{2} The nickel deposit should not be thicker than 0·01 mm. If a thicker deposit is required it is preferable to apply first a thin deposit of nickel, then a deposit of copper 0·02 mm. thick, and then a further deposit of nickel. [See, further, *J. Soc. Chem. Ind.*, 1920, 492A.]   W. G.

Revision of the Atomic Weight of Tin. Electrolytic Estimation of Tin in Tin Tetrachloride. GREGORY PAUL
BAXTER and HOWARD WARNER STARKWEATHER (*J. Amer. Chem. Soc.*, 1920, **42**, 905–917).—The atomic weight of tin has been determined from estimations of tin in stannic chloride. Stannic chloride prepared from very pure electrolytic tin was subjected to a careful fractional distillation, and portions were decomposed under 0·3N-hydrochloric acid, and the solution thus obtained electrolysed, using a mercury cathode which was weighed. The metal obtained from the stannic chloride was shown by means of its spectrum to contain less than 0·001% of lead and copper. Two series of experiments were carried out, the first of which gives a mean of 118·700 for the atomic weight, whilst the second series gives 118·707. The mean value of the atomic weight is therefore 118·703 from sixteen experiments. (Cl = 35·457.)   J. F. S.

Revision of the Atomic Weight of Tin. I. BOHUSLAV BRAUNER and HENRY KREPELKA (*J. Amer. Chem. Soc.*, 1920, **42**, 917—925).—The atomic weight of tin has been determined by the analysis of tin tetrabromide by means of silver, and the ratio $SnBr_4:4Ag$ obtained; four experiments were carried out, three of which are in good agreement, and yield a mean value of 118·70 for the atomic weight ($Br = 79·916$). The fourth experiment is discarded because of an impurity in the silver nitrate used. Other methods are investigated, (i) the oxidation of tin with nitric acid; this method is useless because of absorbed products in the metastannic acid formed; it yields 118·02, which increases to 118·66 when the stannic oxide is fused with potassium hydrogen sulphate. The electrolysis of diammonium stannic chloride gives a value 119·03, which is too high because of difficulties in the complete reduction of the cathode deposit after heating. The synthesis of stannic bromide was found to be unworkable on account of the difficulty in estimating the excess of bromine in the stannic bromide.

J. F. S.

Revision of the Atomic Weight of Tin. II. HENRY KREPELKA (*J. Amer. Chem. Soc.*, 1920, **42**, 925—928. Compare preceding abstract).—A further series of atomic weight determinations for tin. The method was a determination of the ratio $SnBr_4:4Ag$. Greater precautions were taken to exclude moisture from the stannic bromide. The mean value of the ratio $SnBr_4:4Ag$ is found from six experiments to be 1·01586, the extreme values being 1·01580 and 1·01592. From this the atomic weight $118·699 + 0·016$ is calculated. J. F. S.

A New Series of Complex Compounds: Antimonyoxy-iodides. A. C. VOURNAZOS (*Compt. rend.*, 1920, **170**, 1256—1259). —When antimony tri-iodide is decomposed by water to give antimony oxyiodide there is an indication of the intermediate formation of an unstable complex acid, $H(SbOI_3)$. In support of this view it has been possible to prepare the corresponding mercury and copper salts. When antimony tri-iodide and mercuric cyanide in equimolecular proportions are warmed in moist amyl alcohol on a water-bath for four to six hours *mercury antimonyoxyiodide*, $Hg(SbOI_3)$, m. p. 78°, is obtained. This compound is decomposed by concentrated acids, but can be recrystallised from cold dilute hydrochloric acid. It is decomposed by alkali hydroxides. With copper acetate under similar conditions antimony tri-iodide gives *copper antimonyoxyiodide*, $Cu(SbOI_3)$.

If mercury cyanide and antimony tri-iodide are heated together in dry xylene, *mercury antimonyiodocyanide*, $Hg[Sb I_3(CN)_3]$, is obtained, which, when treated with moist amyl alcohol, gives the antimonyoxyiodide described above. If the heating in xylene is continued, a *trimercury antimonyiodocyanide*, $Hg_3[Sb I_3(CN)_3]$, is obtained. Under similar conditions, cuprous cyanide yields *cuprous antimonyiodocyanide*, $Cu_3[Sb_2I_6(CN)_6]$.

W. G.

The Mathematical Possibility of Increasing the Yield or of Reducing the Proportion of the Reacting Substances in certain Chemical Reactions. II. ANGEL PEREZ HERNANDEZ (*Anal. Soc. Quim. Argentina*, 1918, **6**, 306—322).—The author's method (this vol., ii, 107) is further illustrated by application to the equation $Sb_2S_3 + 8KNO_3 + 3C_2 = Sb_2 + 3K_2SO_4 + K_2CO_3 + 4CO_2 + CO + 4N_2$.   W. R. S.

The Properties of Mixtures of Selenium and Antimony. H. PÉLABON (*Ann. Chim.*, 1920, [ix], **13**, 121—153).—A microscopic examination of mixtures of selenium and antimony fused together shows that, for certain proportions of the constituents, the liquid mixture may be formed of two phases, the densities of which are nearly equal, and that the only compound that can be obtained in the pure state by direct fusion of the two elements is the selenide, Sb_2Se_3. A study of the *E.M.F.* of solution of these alloys shows that it increases at first with the time, and finally tends towards a constant value. This value will vary with the relative proportions of antimony and selenium present, and if the *E.M.F.*'s are plotted against the antimony content there is a sharp inflexion corresponding with the selenide Sb_2Se_3. All alloys richer in antimony than the selenide Sb_2Se_3 give piles sensitive to light, the *E.M.F.* rising sharply on illumination and then dropping slowly, the drop becoming sharp when the source of light is removed. The red rays are the most active in promoting this effect.

With a pile in open circuit the *E.M.F.* diminishes gradually with rise in temperature, but in closed circuit the *E.M.F.* increases rapidly as the temperature rises.

Curves are given showing the variations in the resistance and thermoelectric power of mixtures of antimony and selenium with variations in composition and temperature.   W. G.

Bibliography of the Metals of the Platinum Group. Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium, 1748-1917. JAS. L. HOWE and H. C. HOLTZ (*U.S. Geol. Survey, Bull.*, 1919, **694**, 454 pp.).

CHEMICAL ABSTRACTS.

Mineralogical Chemistry.

The Oxidation of the Ingredients of Banded Bituminous Coal. Composition of Coal. FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (T., 1920, **117**, 794—801).

Analysis of a Pyrargyrite. CARLOS CASTRO (*Bol. Min. Mexico*, 1919, **7**, 275—277).—The pyrargyrite analysed came from Union de Providencia, San Felipe, State of Guanajuato, Mexico. The

crystals were separated from matrix and pulverised, and the sulphide mineral was decomposed by heating in a current of chlorine. The mineral consisted of: pyrargyrite, 98·34; argentite, 1·61; pyrite, 0·37%, of which the pyrargyrite was represented by: S, 17·40; Sb, 22·13; Ag, 58·81%. CHEMICAL ABSTRACTS.

Bäckströmite, an Orthorhombic Modification of Mn(OH)$_2$.

G. AMINOFF (*Geol. För. Förh.*, 1919, **41**, 473—491).—Black orthorhombic ($a:b:c=0·7393:1:0·6918$) crystals, occurring with pyrochroite in the calcite veins at the Långban mines, Sweden, are believed to represent a new modification of manganous hydroxide, to which the name *bäckströmite* is given. In composition, however, they are near to manganite, as shown by the following analyses by R. Mauzelius:

	Mn$_2$O$_3$.	MnO.	O.	MgO.	CaO.	PbO.
I.........	77·80	11·59	—	1·68	0·14	0·04
II.........	—	—	8·19	2·31		trace

| | | | | H$_2$O | H$_2$O | |
		Sb$_2$O$_3$.	Fe$_2$O$_3$.	(+130˙).	(−130˙).	Total.
I.....................		0·07	0·14	5·16	3·24	99·86
II.....................		trace	0·43	8·59	3·54	—

Other determinations gave: O (in excess of MnO), 8·15, 8·67; H$_2$O (+130°), 9·05, 8·57; H$_2$O (−130°), 3·27, 3·65%. A partial analysis of the associated, altered pyrochroite gave: O, 8·26; H$_2$O (+130°), 8·31; H$_2$O (−130°), 3·94%. The crystals are often encrusted with a regular intergrowth of pyrochroite, the rhombohedral modification of manganous hydroxide; and Röntgenograms on the face (010) are identical with those on the face (111) of pyrochroite. It is therefore concluded that the crystals represent double pseudomorphs, the change being bäckströmite → pyrochroite → manganite. Other compounds of the type R″(OH)$_2$ belonging to this isodimorphous series are the rhombohedral Mg(OH)$_2$ (brucite), Ca(OH)$_2$, and Cd(OH)$_2$, and the orthorhombic Ca(OH)$_2$ and Zn(OH)$_2$. L. J. S.

Sphenomanganite from Langban, Sweden. GUST. FLINK

(*Geol. För. Förh.*, 1919, **41**, 329—336). Crystals of manganite, D 4·29, exhibiting a sphenoidal habit, but otherwise identical with ordinary manganite, gave on analysis by Mauzelius:

	Mn$_2$O$_3$.	MnO.	O.	Fe$_2$O$_3$.	MgO.	BaO.	H$_2$O.	Total.*
I..........	—	79·60	8·76	0·35	0·87	—	10·16	100·22
II..........	81·1	8·1	—	0·7	0·6	1·6	7·3	99·4

* Incl. SiO$_2$ 0·11, Sb$_2$O$_3$ 0·25, CaO trace, PbO 0·10.

CHEMICAL ABSTRACTS (L. J. S.)

Chubutite and the meaning of its Discovery. E. RIMANN

(*Anal. Soc. Quim. Argentina*, 1918, **6**, 323—328). The author points out that lead oxide is dimorphous, as it crystallises in the tetragonal and rhombic systems (Larsen, *Amer. Min.*, 1917, **2**, 18), whilst the known oxychlorides of lead crystallise as follows:

penfieldite, $PbO,2PbCl_2$, hexagonal; matlockite, $2PbO,2PbCl_2$, tetragonal; mendipite, $4PbO,2PbCl_2$, rhombic; pseudomendipite, $6PbO,2PbCl_2$, rhombic; lorettoite, $13PbO,2PbCl_2$, and chubutite, $14PbO,2PbCl_2$, tetragonal. It is suggested that the oxychlorides of lead form a continuous series, and that the dimorphism of lead oxide persists in the mixed crystals, although the dimorphous modifications of one and the same oxychloride have not yet been observed. The determination of the optical constants and the melting points of the oxychlorides should be helpful towards elucidating the question.

W. R. S.

Baryto-celestine and the Relation of Anhydrite to Celestine and Barytes. WERNER GRAHMANN (*Jahrb. Min.*, 1920, 1, 1—23).—To elucidate the isomorphous relationships between anhydrite, celestine, and barytes, the thermal method was applied to determine how the transition point of each substance is affected by admixture with one of the others, whilst density determinations of the mixtures were also made. The transition points of the pure substances are: calcium sulphate, 1193°; strontium sulphate, 1152°; barium sulphate, 1149°. For the experiments, the pure sulphates were ground together in the desired proportions and heated in a platinum crucible to a few degrees above the transition point. The cooling curve was then followed by means of a platinum-platinum-rhodium couple. The condition diagrams for the three binary systems are given. Strontium and barium sulphates are miscible in all proportions in both α- and β-forms, and baryto-celestine is therefore a true isomorphous mixture. Calcium and strontium sulphates are completely miscible in the α-form above the transition temperature, but in the β-form they are isodimorphous. Addition of strontium sulphate to calcium sulphate first raises the transition temperature up to about 20 mols. % $SrSO_4$; then up to 80 mols. % the transition temperature gradually falls to a minimum at 1010°. The saturated β-mixed crystals co-existing at the eutectic temperature contain 55 to 82 mols. % $SrSO_4$. The density curves indicate that the form of strontium sulphate isomorphous with anhydrite should have a density of 3·55, whilst the second form of calcium sulphate should have a density of 3·29. Barium sulphate and calcium sulphate are likewise isodimorphous, and their miscibility is slight, at most 5 mols. % of calcium sulphate in the barium sulphate crystals. The compositions of naturally occurring minerals are in full agreement with the experimental results, and it is suggested that the name baryto-celestine should be confined to minerals containing between 10 and 90 mols. % of barium or strontium sulphate.

E. H. R.

Aluminium Sulphate from Chile. ATILIO A. BADO (*Bol. Minero Soc. Nac. Min. (Chile)*, 1919, 31, 196 197). A white, fibrous mineral, referred to keramohalite, gave:

Al_2O_3.	CaO.	K_2O.	Na_2O.	SO_3.	H_2O.
17·76	0·05	trace	0·39	37·38	44·77

A small part (0·367%) of the sulphuric acid is free. According to *Anal. Soc. Cient. Argentina*, **73**, 351, this analysis corresponds with 54·70% $Al_2(SO_4)_3$, and the formula is $Al_2O(SO_4)_2,12H_2O$. This appears to be identical with the basic sulphate investigated by Marguerite (*Compt. rend.*, 1880, **90**, 1354). The mineral forms rhombohedral crystals, and is readily soluble in water. It undergoes hydrolysis in dilute solution, and is capable of coagulating suspended matters.   CHEMICAL ABSTRACTS (L. J. S.).

A **New Mineral from Katanga.** G. CESÀRO (*Ann. Soc. Géol. Belgique*, 1912, **39**, *Bull.* 241; Annexe to vol. 39, *Publ. relatives au Congo Belge*, 41—48).—Crusts of minute, blue or greenish-blue crystals are found on limestone and sandstone in the Étoile du Congo copper mine. The crystals are orthorhombic, with $a:b:c = 0·9844:1:0·7679$ or $0·9771:1:0·7872$; H 5½, *n* about 1·7, birefringence about 0·120, 2E 55°, optically negative. Qualitative tests show it to be a copper cobalt phosphate, and from the similarity of the crystallographic and optical properties to those of libethenite, olivenite, etc., the formula is probably

$$(Cu.Co)(OH)PO_4.$$
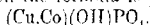
For this mineral the name *cornetite* has been proposed by H. Buttgenbach (*Les Minéraux et les Roches, Liège*, 1916).
CHEMICAL ABSTRACTS. (L. J. S.)

Amblygonite from Ütö. HELGE BACKLUND (*Geol. Foren, Förh.*, 1918, **40**, 757—775).—The mineral had D 3·065, α 1·5910, β 1·6046, γ 1·6125, 2V about 80°. $p > r$. The analysis by Sahlbom gave:

SiO_2.	P_2O_5.	Al_2O_3.	Na_2O.	Li_2O.	F.	H_2O.	Total.
3·50	43·40	33·54	2·71	7·84	11·10	2·18	104·27

CHEMICAL ABSTRACTS.

Meta-torbernite I, its Physical Properties and Relation to Torbernite. A. F. HALLIMOND (*Min. Mag.*, 1920, **19**, 43—47). —"Torbernite" from Gunnislake, Cornwall, suffered no loss in weight over 55% sulphuric acid at the ordinary temperature, but over concentrated acid it slowly lost water, amounting to 10·1% after more than a year. This material is really meta-torbernite I (A, 1916, ii, 258), differing from the torbernite hitherto examined (which has D 3·22; refractive indices, ω 1·592, ε 1·582; axial ratio, $a:c = 1:2·97$). This natural meta-torbernite I has D 3·683, 3·700, ω 1·623, ε 1·625 (N. L. Bowen, 1919), and $a:c = 1:2·28$. When torbernite, D 3·219, is converted into meta-torbernite I by heating under water for several hours at 100°, the density changes to 3·67, and there is a loss in weight of 7·11%, corresponding with the change from $Cu(UO_2)_2(PO_4)_2,12H_2O$ to $Cu(UO_2)_2(PO_4)_2,8H_2O$. The first formula represents torbernite and the latter meta-torbernite I. A morphotropic relation exists between the crystals of the two substances, and the extra four molecules of water are held in layers that alternate with basal layers having the con-

stitution of meta-torbernite I. From the molecular volumes, it is calculated that this extra water has a density of 1·2 in the crystal.

L. J. S.

Pyrobelonite, a New Lead-Manganese Vanadate from Langban, Sweden. GUST. FLINK (*Geol. För. Förh.*, 1919, **41**, 433—447).—This new mineral forms deep-red crystals with adamantine to sub-metallic lustre, which are orthorhombic ($a:b:c = 0.8040:1:0.6509$) with prismatic or acicular habit. It is brittle, without cleavage; H 3½, D 5·377. Associated minerals are hausmannite, barytes, barysilite, pyrochroite, etc. Analyses by Mauzelius gave (Mn : Pb = 7 : 4):

	V_2O_5.	P_2O_5.	PbO.	FeO.	MnO.	MgO.	CaO.	H_2O.	SiO_2.
I.	19·81	0·05	48·99	0·51	25·03	0·66	0·62	n.d.	0·22
II.	20·26	—	48·74	0·48	24·99	0·53	0·92	n.d.	0·22

The crystallographic and optical characters show a relation to those of descloizite.   CHEMICAL ABSTRACTS (L. J. S.).

Gearksutite at Gingin, Western Australia. EDWARD S. SIMPSON (*Min. Mag.*, 1920, **19**, 23—39).—This rare mineral, previously known only in granite-pegmatite at three localities, has been found as small nodules embedded in Cretaceous greensand at Gingin, forty miles north of Perth. It is white, earthy, and very friable. Under the microscope, it shows minute, angular particles, which are birefringent and have refractive index about 1·445. D 2·710—2·720. Associated minerals are phosphatic nodules, glauconite, kaolinite, halloysite, calcite, limonite, quartz grains, and some organic matter; gibbsite [$Al(OH)_3$] is also found in an underlying shale. Analysis I is of the greensand matrix freed from any visible gearksutite. II. by H. BOWLEY, of a dark grey, phosphatic nodule consisting of fluorapatite (57·7%) with calcite (11·4%) and included glauconite, quartz (15%), microcline, and organic matter. III of fossil wood petrified by apatite from greensand at Dandarragan (fifty miles north of Gingin), where it is associated with dufrenite and some vivianite and wavellite. IV, by H. BOWLEY, of gearksutite.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
I.	59·79	8·15	10·47	0·33	nil	2·96	2·32	2·84
II	17·83	2·24	2·26	—	—	40·60	1·60	1·10
III.	1·26	trace	1·01	—	0·78	53·88	1·17	

	Na_2O.	H_2O. —	H_2O. +	CO_2.	P_2O_5.	F.	Organic.	Total less O for F.
I.	0·17	5·17	4·73	0·25	1·72	0·77	0·42	99·86*
II.	0·66	0·04	2·11	5·02	24·80	2·94	0·48	99·84
III.	—	0·22	0·80	1·31	38·80	3·00	0·18	101·16†

	Al.	Ca.	K.	Na.	F.	H_2O. —	H_2O. +	O.	Total.
IV	15·38	22·13	0·06	0·06	41·26	0·12	15·88	[4·88]	100·00‡

* Incl. TiO_2 0·09.   † Incl. Cl 0·01.

‡ Incl. Fe_2O_3, 0·03; K_2O, 0·01, present as glauconite; quartz, 0·19; P_2O_5, trace.

Gearksutite is readily soluble in cold dilute acids, and the solution etches glass. It is decomposed by a hot dilute solution of sodium hydroxide. No water is lost below 270°, and less than one-fifth at 300°; at 320° the loss is 14·00%. Heated rapidly to a red heat, it gives off hydrofluoric acid in addition to water. Analysis IV corresponds with 86·5 molecular % of

$$CaF_2,AlF_2\cdot OH,H_2O,$$
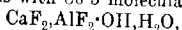
with 13·5 molecular % of $CaF_2,AlF(OH)_2,H_2O$. The genesis of the mineral is discussed and equations given. In granite-pegmatite it is of pneumatolytic origin; hydrogen fluoride acting on the felspars of the rock gives, in the first place, normal anhydrous salts (cryolite, etc.), and later, with the cooling of the solution, normal hydrous salts (pachnolite and thomsenolite), and, lastly, basic salts (gearksutite, topaz, etc.). In the sedimentary rock at Gingin, the mineral has evidently been produced by the action of carbonated water on fluorapatite and gibbsite.

L. J. S.

Meteoric Iron from Yenberrie, Northern Territory of Australia. JOHN C. H. MINGAYE (J. Washington Acad. Sci., 1920, 10, 314—316).

—A mass weighing about 291 lb. was found in 1918 embedded in sandy soil about twenty miles S.S.E. of Yenberrie. The structure is that of a coarse octahedrite with very thin plates of taenite. Anal. I is of the metallic portion, D 7·304. Duplicate determinations gave Ni + Co 7·46, P 0·195, C 0·065. In 100 grams of the iron 0·00026 gram of platinum was found. Tin and gold could not be detected. II is of a black, brittle material found coating pieces of metal from a dark nodule in the centre of the mass. This consists mainly of sulphide and phosphide. III of small, brown plates and laths, extremely brittle and strongly magnetic. It consists largely of schreibersite with magnetite and carbon.

	Fe.	Ni.	Co.	Cu.	P.	S.	C.
I.	92·35	5·98	1·43	0·017	0·161	trace	0·073
II.	65·38	6·10	0·37	trace	4·14	13·06	4·94
III.	73·22	6·35	0·25	0·02	5·02	nil.	2·51

	Cl.	SiO₂.	Cr.	Mg.	O.	Total.
I.	0·003	0·140			—	100·154
II.	0·08		0·23	nil	5·70	100·00
III.	n.d.	0·28	0·20	0·07	12·08	100·00

L. J. S.

Rhythmic Tubular Rust Formation in Meteoric Iron from Cañon Diablo. K. ENDELL (Kolloid. Zeitsch., 1920, 26, 215—217).

—In specimens of meteoric iron, rust (ferric oxide and hydroxide) is found, which penetrates into the iron mass in the form of a tube which exhibits a rhythmic structure. The formation is held to be due to the setting up of local electric currents when the mass is moist, whereby ferrous hydroxide is first formed; this is oxidised, and the ferric hydroxide is deposited. J. F. S.

Analytical Chemistry.

Theory of Gravimetric Analysis, with Special Reference to Sources of Error. L. MOSER (*Zeitsch. anal. Chem.*, 1920, **59**, 1—10).—A discussion on the accuracy of general gravimetric methods. Errors which cannot be eliminated completely are those due to solubility of precipitates, induced precipitation, formation of solid solutions, and adsorption, occlusion, and inclusion. Other sources of error, more under control, are those due to the action of atmospheric oxygen or carbon dioxide on the precipitate, contamination from glass vessels, and decrepitation or partial volatilisation during ignition. The different errors may have a compensating effect. W. P. S.

Yellow Light in Polarimetric Determinations. LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 497—499). —To obviate the drawbacks of the use of sodium chloride, Dupont (A., 1897, ii, 77) proposed a mixture of salt and trisodium phosphate; this is found to work very satisfactorily. For its preparation, 1 gram-molecule of disodium phosphate is dissolved in water and treated with 1 gram-molecule each of sodium hydroxide and chloride. The solution is evaporated to dryness and the residue fused. W. R. S.

Colorimetric Estimations with Solutions containing Two Coloured Substances. K. GEORGE FALK and HELEN MILLER NOYES (*J. Biol. Chem.*, 1920, **42**, 109—130).—The authors have examined with much care the principles underlying the ordinary use of the colorimeter for quantitative work, particularly in such cases as the Benedict method for the estimation of dextrose, where two coloured substances are present. From this study, it is shown that there is grave danger of the introduction of serious errors in such methods unless the standard and the unknown solutions are nearly alike in composition and concentration. J. C. D.

A Photographic Turbidimeter. W. G. BOWERS and JACOB MOYER (*J. Biol. Chem.*, 1920, **42**, 191—198).—The apparatus, which is described and illustrated, is fashioned so that a strong light is passed through a definite and comparatively narrow column of the substance in question, and what is not lost falls on one side of an oil spot on paper. On the other side of the spot falls a beam of light of equal initial intensity, in the path of which standardised ground glass disks are inserted until equality of illumination is obtained. J. C. D.

Decomposition (or Removal) of Ammonium Sulphide in Qualitative Analysis. F. FEIGL (*Zeitsch. anal. Chem.*, 1920, **59**, 12—15).—When a solution containing ammonium sulphide is warmed with the addition of a slight excess of lead hydroxide and filtered, a clear filtrate is obtained which is free from lead and

sulphur. This method is preferable to the usual procedure for removing excess of ammonium sulphide (acidifying and boiling to expel hydrogen sulphide), since colloidal sulphur is not formed and there is no danger of oxidising a portion of the sulphur, with the formation of sulphuric acid, which would interfere with subsequent tests for alkali earths.　　　　　　　　　　　W. P. S.

Estimation of Bromine. F. WÜNSCHE (*Arch. expt. Path. Pharm.*, 1919, **84**, 328—339).—In order to estimate bromine in organic matter, the substance is dried with sodium peroxide in a nickel basin, first on a water-bath, then on a free flame, and eventually incinerated. The ash is extracted with distilled water and filtered, and the filtrate neutralised with concentrated sulphuric acid and treated with potassium permanganate and sulphuric acid. The free bromine is carried over by means of a current of air into a vessel containing a known volume of magenta and sulphurous acid. The bromine is then estimated colorimetrically by comparing the violet coloration which is produced with a set of standards. Two mg. of neuronal were estimated in 30 c.c. of blood with an error of 12%. Neuronal, adaline, and bromural were estimated in frog's tissue by this method with an error of about 7%.　　　　　　　　　　S. S. Z.

Kendall's Method of Estimating Iodine in Thyroid Preparations. S. B. KUZIRIAN (*Proc. Iowa Acad. Sci.*, 1918, **25**, 495—496).—(1) In destroying organic matter, it is advantageous to use more sodium hydroxide and less potassium nitrate to obviate the formation of large quantities of nitrite, which tend to liberate iodine. (2) Organic substances with high ash content often contain iron or some other interfering element, which ought to be eliminated before trustworthy results can be obtained. Filtration at this point does not altogether eliminate the interfering action of ash. When, however, the sodium hydroxide fusion was taken up with hot water, a few grams of sodium carbonate and some talc added, and the solution brought to boiling and kept boiling for a few minutes, set aside for two hours, and filtered, the filtrate was free from interfering basic elements. (3) In acidifying the above filtrate with 85% syrupy phosphoric acid, the author's experience was well in accord with that of Forbes, Beegle, and others, who found that one or two drops of phosphoric acid in excess was insufficient to assure expulsion of all bromine. Even after the addition of 1·5 to 2 c.c. in excess, the whole of the bromine could be boiled off without causing any loss of iodine. This was shown by taking an aliquot of accurately standardised alcoholic solution of iodoform and estimating iodine according to Kendall's method. No loss of iodine occurred when 2 c.c. of acid were added in excess. (4) In boiling off the bromine, it was made a practice to dilute the filtrate to more than 400 c.c. and boil down to 250 c.c., thus assuring a complete expulsion of bromine. Under these conditions, the author found the method applicable

for tankage, roughage, and other organic substances with a high
per cent. of ash.   CHEMICAL ABSTRACTS.

**Modifications in the Technique of Estimating Oxygen
in Blood with Van Slyke's Apparatus.** E. P. POULTON (*Proc.
Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxi. Compare A., 1918,
ii, 82).—Modifications have been introduced which avoid certain
errors due to the presence of dissolved air in the reagents, and
which shorten the estimation. Ten c.c. of dilute ammonia are
shaken with some crystals of potassium ferricyanide, a trace of
saponin, and four or five drops of octyl alcohol. The mixture is
placed in the cup and drawn completely into the apparatus, and
sealed with mercury. By reducing the pressure, the dissolved air
is withdrawn from the reagent, which is then returned to the cup.
The blood pipette has a small ring of fine rubber tubing round
the tip. By this means, the pipette, when full of blood, is pressed
down beneath the ferricyanide mixture on to the bottom of the
cup, and on turning the upper tap of the apparatus, the blood is
delivered directly into the burette without admixture with the
reagent. On removing the pipette, the last portion of the blood
is washed in by the ferricyanide mixture, 2 or 3 c.c. of the latter
being allowed to remain behind in the cup. The tap is then
sealed with mercury.   J. C. D.

**Detection of Water in Alcohol and other Organic
Solvents.** F. HENLE (*Ber.*, 1920, **53**, [*B*], 719—722).—When
normal aluminium ethoxide is heated at about 340° until the
temperature, as indicated by an immersed thermometer, begins to
fall, it yields a heavy, yellow, semi-solid mass, the composition
of which corresponds with the formula $Al_2(OEt)_4O$; if the action
is continued until the thermometer indicates 330° or less, a brittle,
yellow resin is obtained, which has the approximate composition
$Al_4(OEt)_6O_3$. Both substances are soluble in xylene and are suit-
able for the detection of water, the latter compound being the
more sensitive. The reagent may be readily prepared in a single
operation by treating aluminium turnings with absolute alcohol
and a little mercuric chloride, heating the product for several
hours on the water-bath until the aluminium ethoxide appears
dry, distilling off the alcohol of crystallisation at 210—220°, and
finally heating the crude aluminium ethoxide at about 340° for
an hour. The product is dissolved in about a litre of dry xylene
and the solution filtered through a dry paper. The clear, pale
yellowish-brown filtrate can be preserved indefinitely in the
absence of moisture and air. The test is carried out by adding
a few drops of the xylene solution to a few c.c. of the liquid under
investigation; according to the quantity of water present, a
voluminous, gelatinous precipitate of aluminium hydroxide is pro-
duced immediately or after a few seconds. Distinct evidence is
obtained in the various cases, with the percentage of water enclosed
in brackets after the name of the solvent: ethyl alcohol (0·05),
methyl alcohol (0·1), ethyl ether (0·005), ethyl acetate (0·1), acet-

aldehyde (0·1), acetone (1). The two substances last named may also yield a white turbidity, due to the precipitation of excess of the ethoxide, which, however, may readily be distinguished from aluminium hydroxide, as it readily dissolves in xylene or in an excess of the reagent. H. W.

Oxidation in Relation to the Estimation of Sulphites.
H. I. WATERMAN (*Chem. Weekblad*, 1920, **17**, 196—197).—The oxidation of sulphite solutions in air, as measured by the increasing volume of the solution required to reduce a given quantity of iodine, proceeds fairly rapidly in the case of sodium hydrogen sulphite and very rapidly in the case of normal sodium sulphite, the hydroxyl ions present in the latter being probably catalytically active. Addition of sodium hydroxide accelerates the oxidation. Accurate estimations of sulphite were obtained by dissolving the salt in a boiled 5% glycerol solution in a flask filled with carbon dioxide. A measured quantity of this solution is run into excess of acid standard iodine solution, also under carbon dioxide, and the residual iodine titrated with thiosulphate. W. S. M.

An All-glass Nitrogen Apparatus. E. R. ALLEN and B. S.
DAVISSON (*Ann. Missouri Bot. Gardens*, 1919, **6**, 45—48).—The apparatus is of the usual Kjeldahl form. The advantages claimed are: the elimination of rubber connexions; efficient scrubbing of entrained alkali from the steam; the use of Pyrex glass, which does not yield an appreciable amount of alkali to steam or to boiling solutions. The rigidity may be lessened by one rubber connexion between the distilling bulb and the Kjeldahl flask if the glass ends are kept close together. The distilling bulb has a capacity of 200 c.c.; steam enters it through a re-curved tube with a perforated end. Thus the bulb acts as a trap for scrubbing the steam. CHEMICAL ABSTRACTS.

1. Modified Kjeldahl Method. 2. Carbazole Test for Nitrites. 3. Colour Test for Tryptophan in Urine.
W. A. FEARON (*Dub. J. Med. Sci.*, 1920, [iv], No. 1, 28–32; from *Physiol. Abstr.*, 1920, **5**, 79).—(1) The best proportion of the constituents in the acid mixture for incineration is given. Steam distillation is best, but Cole's method of distilling with alcohol is also good and rapid. Methyl-red is recommended as an indicator. (2) All urines give a colour with sulphuric acid, but the tint varies from orange vermilion to deep violet; a large number of substances might give colours: (*a*) pigments and chromogens from bile and blood, and (*b*) from indole and derivatives from intestinal putrefaction which reach the urine via the blood. The red colour is attributed to indole derivatives reacting with the α-nitro-group. Nitrites give a green colour with carbazole. (3) The usual tests are not adequate to detect tryptophan in urine, because of the presence of other indole compounds. If the urine is treated with an excess of the Hopkins-Cole reagent and a drop of the mixture is added to concentrated sulphuric acid, the tryptophan condensation

product (allied to carbazole) gives a deep green colour with the nitrites of urine. Tryptophan in urine is rare.   J. C. D.

Sensitive Reaction for Nitrites. P. H. HERMANS (*Pharm. Weekblad*, 1920, **57**, 462—463).—The following gives a sensitive reaction for nitrite in presence of nitrate. To 2 c.c. of the solution to be tested a few drops of glacial acetic acid are added, and then 2 c.c. of 5% potassium oxalate solution, 1 c.c. of 5% manganous sulphate solution, and a few drops of 3% hydrogen peroxide. A red coloration indicates nitrite. 0·02 Gram of sodium nitrite per litre can be detected in this way.   W. S. M.

Detection of Arsenic in Sulphur. HAROLD S. DAVIS and MARY D. DAVIS (*J. Ind. Eng. Chem.*, 1920, **12**, 479—480).—Schaeppi's method of detecting arsenic in sulphur (extraction with warm ammonia and treatment of the solution with silver nitrate to precipitate the dissolved sulphide) is untrustworthy, since sulphur itself dissolves in ammonia, and the resulting ammonium sulphide gives a precipitate of silver sulphide. The best method consists in oxidising the sulphur with bromine and nitric acid, and applying the Gutzeit test to the residue.   W. P. S.

Iodometric Estimation of Arsenic Acid. P. FLEURY (*J. Pharm. Chim.*, 1920, [vii], **21**, 385—391).—The reaction $As_2O_5 + 4HI = As_2O_3 + 2I_2 + 2H_2O$ is complete in five minutes when the reacting mixture is heated at 100° and contains 25% of potassium iodide and 3·65% of hydrogen chloride. A quantity of arsenate equivalent to about 50 c.c. of $N/10$-iodine solution is dissolved in 30 c.c. of water, 3 c.c. of hydrochloric acid (D 1·171) are added, and the mixture is heated on a boiling water-bath for five minutes; 25% of potassium iodide is then added, the heating continued for a further five minutes, and, after the mixture has been cooled, the iodine is titrated with $N/10$-thiosulphate solution. Owing to the action of dissolved oxygen on hydriodic acid, the amount of iodine is always larger than that which should correspond with the arsenic acid. An excess of sodium hydrogen carbonate is then added to the mixture and the arsenious acid titrated with $N/10$-iodine solution.   W. P. S.

[**Estimation of Arsenic Acid in Presence of Arsenious Acid.**] GEORG JOACHIMOGLU (*Arch. expt. Path. Pharm.*, 1916, **80**, 8—24).—See this vol., i, 510.

Spectroscopic Methods for Estimating Carbon Monoxide in Blood. H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxvii—lxxviii).—The most satisfactory method was found to be one previously described by the author (A., 1912, ii, 488).   J. C. D.

The Estimation of Carbon Dioxide and Fermentable Sugars. ARTHUR SLATOR (*J. Soc. Chem. Ind.*, 1920, **39**, 149—151T) —The estimation of carbon dioxide is carried out as follows. The

carbonate solution is placed in a distillation flask connected through the neck opening to a trap leading to a condenser and receiver containing standard barium hydroxide solution. To the side-arm of the distillation flask is connected by means of pressure tubing a small tube containing dilute sulphuric acid. The pressure tubing is clipped, while the whole apparatus is being exhausted, the clip then removed, and the acid in the small tube is boiled over into the distillation flask. The solution in the latter is then boiled, and the carbon dioxide absorbed by the barium hydroxide is determined by titration. The apparatus has been used for determining the quantity of carbon dioxide produced during the fermentation of sugars. The fermentation was allowed to proceed in a small tube sealed off at a fine capillary. The tube was then connected to the side-arm of the distillation flask by pressure tubing, the apparatus was exhausted, the capillary tube broken, and the carbon dioxide boiled over into the receiver. The method serves to characterise enzymes and yeasts by fermenting with them appropriate sugars.   E. H. R.

Analysis of Silicate and Carbonate Rocks. W. F. HILLEBRAND (*U.S. Geol. Survey, Bull.* **700**, 1919, 1—285).—The Bulletin is a general treatise on the analysis of rocks; methods are described for the separation and estimation of the common and rare constituents of the rocks, and only those methods which have been found to be trustworthy are recommended. Attention is directed to the frequent occurrence of boron in rocks, but hitherto the estimation of this element has usually been neglected; Chapin's method (A., 1909, ii, 93) is recommended for the purpose.
                                                                W. P. S.

The Analysis of Natural Silicates. LOUIS DUPARC (*Bull. Soc. franç. Min.*, 1919, **42**, 138--241; from *Chem. Zentr.*, 1920, ii, 680).—A summary and extension of many scattered communications by the author and his pupils on this subject. The work comprises a critical re-examination, discussion, and frequently modification of practically all the important methods of silicate analysis.   H. W.

Practical Methods for the Estimation of Radium. III. α-Ray Method, γ-Ray Method, Miscellaneous. S. C. LIND (*J. Ind. Eng. Chem.*, 1920, **12**, 469—472. Compare A., 1915, ii, 486; 1916, ii, 114).—The α-ray method is simple and sufficiently trustworthy for many purposes, but it cannot take the place of a direct radium estimation in such minerals as carnotite, pitchblende, etc. Its errors are due to variation in the amount of the loss of radium emanation by gaseous diffusion from the ore, to variation in the radium–uranium ratio, and to the position of the radio-active material in the individual grains of the ore. The γ-method is a convenient means of measuring radium in quantities above 0.1 mg., but the radium preparation must be confined in a closed vessel for one month before the measurement is made, so that the

γ-radiation will have reached a maximum; if the measurement is made earlier a correction must be made for the unelapsed time. Modifications of the interchangeable electroscope (*loc. cit.*) are described.   W. P. S.

The Separation and Gravimetric Estimation of Potassium.

S. B. KUZIRIAN (*Proc. Iowa Acad. Sci.*, 1917, **24**, 547—550).— Aniline perchlorate is the best reagent to replace platinic chloride for the separation and gravimetric estimation of potassium. The best results are obtained when the following points are observed: The exact strength of alcohol used must be known, and none used that runs below 99·5%. For every 1·5 c.c. of water used for dissolving the mixed chlorides, 50 c.c. of absolute alcohol should be used. The solution of a weighed amount of aniline perchlorate in 50 c.c. of absolute alcohol is added to the solution of the mixed chlorides drop by drop with constant shaking and set aside for one to two hours before filtering, to avoid occlusion of potassium chloride. The chief objections to the perchlorate method are the time and the slight solubility of potassium perchlorate in 95% alcohol. The use of aniline perchlorate in place of perchloric acid so shortens the process as to render it more advantageous than any other method in use for the separation and estimation of potassium; moreover, it affords the best means for the direct separation and estimation of sodium in the alcoholic filtrate.
                                                   CHEMICAL ABSTRACTS.

The Carrying Down of Calcium and Magnesium Hydroxides by Precipitates of Ferric Hydroxide. TOPORESCU

(*Compt. rend.*, 1920, **170**, 1251—1253).—A second precipitation with ammonium hydroxide is quite sufficient to remove all calcium hydroxide from a ferric hydroxide precipitate. This may also be effected by washing the first precipitate of ferric hydroxide with a boiling 5% solution of ammonium nitrate. The addition of 2% of ammonium chloride to the solution prior to the precipitation of ferric hydroxide does not prevent it from carrying down some calcium hydroxide. Similarly, it does not prevent the carrying down of magnesium hydroxide, and the latter cannot be removed either by simple reprecipitation of the ferric hydroxide or by washing the precipitate with ammonium nitrate.   W. G.

Estimation of Mercury. C. M. BOUTON and L. H. DUSCHAK

(*U.S. Bureau of Mines, Techn. Paper*, **227**, 1920, 1—41).—The finely powdered mercury ore is mixed with lime and heated in a tube closed at one end. A layer of coarse sand is first placed in the tube, then the mixture, and finally a layer of lime, and the opening closed with a plug of brass wire gauze. The tube is allowed to project 7 to 12 cm. beyond the furnace, which is heated at about 500°. The effect of the sand filling is to reduce the volume of air expelled, and so prevent loss of mercury. In the presence of much sulphur, cupric oxide is mixed with the lime whilst organic matter is oxidised by adding a small proportio

of potassium chlorate to the sand. The distilled mercury is dissolved off the tube by hot nitric acid, and oxidised by means of potassium permanganate, the excess of which is removed with hydrogen peroxide, and the solution titrated with standard potassium thiocyanate solution, with ferric sulphate or nitrate (free from haloids) as indicator. The method is also applicable to mercury in solution, the metal being precipitated as sulphide, and the precipitate treated as described. [See, further, *J. Soc. Chem. Ind.*, 1920, 492A.] C. A. M.

Petersen's Method for the Qualitative Separation of Cations of the Third and Fourth Groups. P. DE PAUW

(*Chem. Weekblad*, 1920, **17**, 191–192).—Various imperfections in Petersen's scheme (A., 1910, ii, 654) are pointed out and discussed. The following alternative scheme is proposed: To the acid hydrogen sulphide filtrate sodium sulphate solution is added, whereby barium, strontium, and calcium (in part) are removed as sulphates. The filtrate contains the ions Fe'', Co'', Ni'', Mn'', Cr''', Al''', Zn'', Ca'', Mg''. This is treated with solid sodium carbonate and sodium hydroxide. Ammonia is boiled off, and sodium sulphide added. All metals except aluminium are precipitated as carbonates, hydroxides, or sulphides. Dilute hydrochloric acid removes Fe'', Mn'', Zn'', Cr''', Ca'', Mg'' as chlorides, leaving nickel and cobalt as sulphides. To this solution is added solid sodium carbonate and sodium hypochlorite. Zinc and chromium form zincoxide and chromate respectively, which may be separated by means of barium chloride. The residue contains ferric hydroxide, hydrated manganese dioxide, calcium and magnesium carbonates. This is treated with 5% acetic acid containing a little phosphate. A solution of calcium and magnesium acetates is obtained. The residue is dissolved in sodium peroxide and nitric oil, and the iron and manganese separated in the usual way.

W. S. M.

Different Methods of Estimation of Manganese and their Use in the Examination of Plant Ashes and Similar Products. D. H. WESTER (*Rec. trav. chim.*, 1920, **39**, 414—422).

For the estimation of small amounts of manganese a colorimetric method is necessary, and of the four methods examined only one, namely that of Marshall (compare A., 1901, ii, 350), in which the manganese is oxidised to permanganate by potassium persulphate, is found to be satisfactory. The presence of small amounts of nitric or sulphuric acid or silver nitrate do not interfere with this method. The amount of persulphate used has no influence. The heating in a water-bath for the oxidation should not exceed thirty minutes. The presence of salts likely to be found in plant ashes does not interfere with the estimation, although it is preferable to remove chlorides by a preliminary evaporation with sulphuric acid. If ferric salts are present to an extent of more than 0·05 g. per 100 c.c., they may make it impossible to carry out the

colorimetric comparison, and thus the method may not always be applicable to the analysis of soils.   W. G.

Separation of Chromium and Manganese. M. HERSCH-KOWITSCH (*Zeitsch. anal. Chem.*, 1920, **59**, 11--12).—The manganese and chromium are oxidised to permanganate and chromate respectively, and their solution is heated on a water-bath for some hours with the addition of ammonium sulphate and an excess of ammonia. The chromate remains unchanged, whilst the whole of the manganese is precipitated; the precipitate is collected, washed with 5% ammonium sulphate solution, then with hot water, ignited, and weighed as Mn_3O_4.   W. P. S.

Separation of Tin and Antimony. Estimation of Tin by Cupferron. A. KLING and A. LASSIEUR (*Compt. rend.*, 1920, **170**, 1112--1114).—The antimony is separated from the tin by precipitation with hydrogen sulphide in the presence of hydrofluoric acid. The antimony sulphide is collected, washed, and redissolved in hydrochloric acid with a little potassium chlorate. The solution is filtered, and the antimony reprecipitated as its sulphide, which is collected, dried at 300° in a current of carbon dioxide, and weighed.

To the filtrate from the first precipitation of the antimony sulphide, boric acid is added, and the liquid boiled with a little hydrogen peroxide. After cooling, a 10% solution of cupferron is added, and the white precipitate which forms is collected, washed with cold water, dried, and calcined, and the tin weighed as stannic oxide. The results obtained by this method are very satisfactory. [See, further, *J. Soc. Chem. Ind.*, 1920, 470A.]

W. G.

Estimation of Ethyl Alcohol in Mixtures of Alcohol, Sulphuric Acid, and Water. G. S. BUTLER and H. B. DUNNICLIFF (*J. Soc. Chem. Ind.*, 1920, **39**, 146--147T).—The free acid, that is, free sulphuric acid plus acidity due to ethyl hydrogen sulphate, is determined by direct titration with standard alkali. The total acid present, including that which has undergone esterification, is determined by evaporating a weighed quantity of the alcoholic sulphuric acid with excess of standard alkali to a pasty consistence, heating in an air oven for half an hour at 120°, extracting with distilled water, and titrating the excess alkali with standard acid. By a simple calculation, from the two determinations, the acid esterified, and hence the alcohol present as ester, can be found. The free alcohol is determined by distillation, followed by a density determination of the filtrate.   E. H. R.

The Action of Hydrocyanic Acid on Dextrose. J. BOUGAULT and J. PERRIER (*Compt. rend.*, 1920, **170**, 1395--1397).—The action of potassium cyanide on dextrose may be used as a means of estimating dextrose if an excess of the cyanide is used and the mixture is left for at least two days at 20° as the action is slow;

The residual excess cyanide may then be estimated, or the change in rotation, from $[\alpha]_D +53°$ of the dextrose to $[\alpha]_D +1·87°$ of the glucoheptonates, may be determined.

If an excess of sugar is used with a deficiency of cyanide, the whole of the cyanide is destroyed in about ten hours at 20°, and the mixture is no longer toxic.   W. G.

An Improved Method for the Estimation of Sugar in the Urine and Blood. P. J. CAMMIDGE (*Lancet*, 1919, 1, 939).— Further experience with the volumetric method for the estimation of sugar (A., 1917, ii, 276) has confirmed the accuracy of the results given with quantities above 0·5%, but with percentages below that amount too low a reading may be obtained unless further precautions than those described are taken against oxidation, especially in warm weather. When a urine is expected to contain a low percentage of sugar, under 0·5%, and with all blood and other fluids containing smaller amounts, the water to which the iodine solution is to be added should be thoroughly boiled, to expel dissolved air, and cooled immediately before the estimation is to be made. It is also advisable that the alkaline copper solution for sugar estimations with urine be boiled in a small conical flask, provided with a loose funnel as a stopper, instead of in a beaker as previously described, and that the required amount of urine be run into the boiling fluid from a pipette when the air dissolved in the solution and contained in the flask has been expelled. With blood, etc., the 7·5 c.c. of filtrate and 1 c.c. of modified Benedict solution are added after they have boiled for a few seconds. The water used for diluting the iodine solution and for washing out the flasks, etc., should have been recently boiled and cooled. With these additional precautions the method gives uniformly trustworthy figures, even with the small amount of sugar in normal urine and blood.   CHEMICAL ABSTRACTS.

Proximate Analysis of Coniferous Woods. W. H. DORE (*J. Ind. Eng. Chem.*, 1920, 12, 476 479). Methods are given for the estimation of loss on drying benzene extract, alcohol extract, cellulose, lignin, soluble pentosans, mannan, and galactan. Preliminary hydrolysis is omitted in the estimation of the cellulose and lignin; soluble pentosans are estimated in the chlorination liquors, and mannan and galactan on separate portions of the original material. Analyses of redwood, yellow pine, and sugar pine show that the sum of the constituents, as found by the above-mentioned methods, is slightly over 100% in every case.
                                                      W. P. S.

Colorimetric Estimation of Lactic Acid in Urine. POLONOWSKI (*Compt. rend. Soc. Biol.*, 1920, 73, 475; from *J. Pharm. Chim.*, 1920, [vii], 21, 449 450). The urine is clarified by adding from 1 to 3% of egg albumin and precipitating this with sodium metaphosphate and dilute sulphuric acid. One c.c. of the clear urine is then treated with 5 c.c. of concentrated sulphuric

acid (added slowly to prevent heating) and 5 drops of a 1% codeine solution (in alcohol), and the yellow coloration obtained is compared with those of standards containing known amounts of lactic acid. The results are trustworthy only when not less than 0·001% or not more than 0·01% of lactic acid is present.   W. P. S.

Identification of the Cinnamic Ion by means of the "Oxyferric" Catalyst [a Ferric Salt + Hydrogen Peroxide].

G. Deniges (*Bull. Soc. pharm. Bordeaux*, 1919, **57**, 209—212).— In the case of free cinnamic acid or a cinnamate, as little as 0·02 gram of the acid in 1 litre of solution can be detected by adding 1 drop of ferric chloride solution to 2 c.c. of the solution to be tested, boiling, and adding 1 drop of hydrogen peroxide (6—10 vols. oxygen), when the odour of benzaldehyde is observed after shaking for about ten seconds. The sensitiveness of the reaction is increased by adding 1 drop of 10% sulphuric acid with the ferric chloride solution; this procedure also serves for the identification of a cinnamate. In the case of a cinnamic ester one drop (if liquid) or several particles (if solid) of the sample is boiled fo twenty to thirty seconds with 6—8 c.c. of dilute sodium hydroxid solution; the solution while hot is acidified with 10% sulphuri acid, 1 drop of ferric chloride solution is added, the mixture i boiled, treated with 1 drop of hydrogen peroxide solution, and again boiled, whereby the odour of benzaldehyde is produced. Thi method also serves to detect the presence of cinnamic acid in complex mixtures, such as Peru and Tolu balsams.

CHEMICAL ABSTRACTS.

Estimation of Salicylic Acid in the Blood and its Action on the Heart.

C. Friderichsen (*Arch. expt. Path. Pharm.*, 1917 **80**, 235—259). A micro-method for the estimation of salicylic acid in blood. The blood is absorbed by a small piece of blotting paper (about 250 mg.), and weighed in a torsion balance. The paper is then introduced into a test-tube, to which 10 c.c. of a boiling solution of calcium chloride containing 1·5 c.c. of 25% hydrochloric acid per litre is added. It is allowed to remain in contact with the solution for three hours. The calcium chloride solution is extracted with ether. The ether is just evaporated on a water bath at 32—33°, and any traces left removed by means of a stream of air. The salicylic acid is dissolved in water and estimated colorimetrically. Employing this method the distribution of salicylic acid in the serum and in the blood corpuscles, as well as the action of various doses on the heart, was studied, the results of which are recorded in the communication.   S. S. Z.

Two Procedures for the Estimation of Alkali Nitroprussides.

Le Her (*Bull. Soc. pharm. Bordeaux*, 1920, **58**, 12—16). —A solution of 1·0 gram of sodium nitroprusside in 50 c.c. of water is filtered and 59 c.c. (*sic*) of the filtrate are neutralised with sulphuric acid and treated with an excess of a ferric salt. The precipitate of Prussian blue is collected, washed with hot water

(these washings are discarded), then several times with a 20% sodium hydroxide solution, and again with water, the combined filtrates containing sodium ferrocyanide are acidified with sulphuric acid and titrated with $0.1N$-permanganate (1 c.c. $= 0.03582$ gram of sodium nitroprusside).

In the second method a solution containing not more than 0.40 gram of sodium nitroprusside is treated in a 100 c.c. flask with 30 c.c. of $0.1N$-silver nitrate, water is added to the mark, and, after shaking, the liquid is filtered and the excess of silver nitrate in the filtrate and washings is estimated by Denigès' silver cyanide method.　　CHEMICAL ABSTRACTS.

Differentiation of Vanillin and Heliotropin. A. LABAT

(*Bull. Soc. pharm, Bordeaux*, 1919, **57**, 259—260). To 2 c.c. of sulphuric acid (D 1.84) are added 0.1 c.c. of an alcoholic solution of vanillin or heliotropin and 0.1 c.c. of an alcoholic solution of gallic acid (20%). and the mixture is boiled on a water-bath for two or three minutes. In the case of vanillin, the liquid will assume a yellowish-brown or brown colour, whereas the liquid containing heliotropin will be coloured blue or emerald-green, depending on the quantity of heliotropin present. This reaction serves to detect heliotropin in quantities as small as 0.00005 mg.　　CHEMICAL ABSTRACTS.

The Nitrosoindole Test. J. GROENEWEGE (*Med. Geneesk. Lab., Welterreden*, 1919, [iii], *A.* 177-193).

The red coloration obtained when a peptone culture of certain bacteria is treated with a drop of mineral acid is due to the presence of nitrate in the peptone, and there is no need to add nitrite before the coloration can be obtained. If the peptone medium is inoculated previously with a denitrifying organism, the nitrate is reduced to nitrite and the latter to ammonia or nitrogen, and the medium no longer yields a nitrosoindole reaction when used for the culture of the organisms mentioned (cholera vibriones, etc.). Conversely, the peptone medium freed from nitrate and nitrite as described may be used for the detection of traces of nitrate; the substance to be tested is added to the medium, which is then inoculated with an organism capable of giving a nitrosoindole reaction. W. P. S.

Analytical Characters of Dimethylaminoantipyrine (Pyramidone). JUAN A. SÁNCHEZ (*Anal. Soc. Quim. Argentina*, 1918, **6**, 422-428, 513-521).

Various oxidising agents impart a violet colour to solutions of pyramidone. The action of iodic acid is quantitative, each atom of oxygen acting on one molecule of pyramidone; when a solution of the base is treated with excess iodic acid, iodine is liberated after a few minutes. By means of this reaction the purity of pyramidone may be determined iodometrically; 0.5, 1, 1.5, 2, 2.5, and 3 c.c. of a 0.1% solution of standard pyramidone are treated in cylinders with water to 3 c.c. bulk, one drop of concentrated sulphuric acid, and 2 c.c. of 1% iodic acid solution. After five minutes, 5 c.c. of chloroform are added to

each tube, and the liquid well shaken. The sample to be tested is treated in the same manner, and the intensity of the violet colour of the liberated iodine in chloroform in each series of tubes compared.

Antipyrine is without action on iodic acid, but absorbs iodine; an admixture of 20% of antipyrine is sufficient to prevent the liberation of iodine by pyramidone. Distillation of pyramidone with ferric chloride or the theoretical amount of iodic acid yields formaldehyde, derived from the oxidation of a methyl group. To detect pyramidone in presence of large quantities of antipyrine, $N/10$-silver nitrate is recommended. This produces after five minutes in the cold, but quickly on warming, an intense bluish-violet coloration.

Pellizzari's reaction (combination of antipyrine with formaldehyde) can be used for the quantitative separation of antipyrine and pyramidone; 5 c.c. of the aqueous solution of the two bases are left for four days with 5 c.c. of formaldehyde, 2 c.c. of hydrochloric acid, and 2 c.c. of water; the liquid is made ammoniacal, when a precipitate of methylenediantipyrine is obtained. The filtrate is treated with chloroform to extract pyramidone.

To detect small quantities of antipyrine in pyramidone, a little of the powder in a porcelain dish is submitted to the action of nitrous fumes from sodium nitrite and sulphuric acid; the antipyrine crystals will acquire a persistent green colour, whilst pyramidone is coloured violet, although only transiently. To prove the presence of pyramidone in coloured or syrupy liquids, 10 c.c. are made alkaline with ammonia and shaken with chloroform. The separated extract is evaporated to dryness, and the residue dissolved in water and tested with silver nitrate. Pyramidone may be titrated with $N/10$-sulphuric acid in presence of methyl-orange, 0·231 gram of pyramidone requiring 10 c.c. of the acid for neutralisation.   W. R. S.

Excretion of Quinine in the Urine. M. NIERENSTEIN (Extract from Observations on Malaria, War Office, 1919, pp. 1—79. Compare A., 1919, i, 236).—The thalleioquinine test can only be regarded as a valuable positive test for quinine, a negative result in no way indicating the absence of the drug. Many other qualitative tests for quinine were investigated, but the only one which is regarded as quite trustworthy is Ramsden and Lipkin's technique for carrying out Herepath's test. Encouraging results were obtained with Robertson's test. In testing for quinine in urine the picric acid test is recommended for clinical use.

The estimation of quinine in urine was studied very completely, and the author obtained the best results with Barratt and York's modification of Giemsa and Schaumann's method. By this method the excretion of quinine was fully studied.   J. C. D.